Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling

Evaluation Number 9

NASA Panel for Data Evaluation:

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ABSTRACT

This is the ninth in a series of evaluated sets of rate constants and photochemical cross sections compiled by the NASA Panel for Data Evaluation. The primary application of the data is in the modeling of stratospheric processes, with particular emphasis on the ozone layer and its possible perturbation by anthropogenic and natural phenomena. Copies of this evaluation are available from the Jet Propulsion Laboratory, California Institute of Technology, Library Section, MS 111-120, 4800 Oak Grove Drive, Pasadena, California, 91109.

CONTENTS

CHEMICAL KINETICS AND PHOTOCHEMICAL DATA

FOR USE IN STRATOSPHERIC MODELING

INTRODUCTION

The present compilation of kinetic and photochemical data represents the ninth evaluation prepared by the NASA Panel for Data Evaluation. The Panel was established in 1977 by the NASA Upper Atmosphere Research Program Office for the purpose of providing a critical tabulation of the latest kinetic and photochemical data for use by modelers in computer simulations of stratospheric chemistry. The previous publications appeared as follows:

Evaluation Number	Reference
1	NASA RP 1010, Chapter 1 (Hudson, 1977)
2	JPL Publication 79-27 (DeMore et al, 1979)
3	NASA RP 1049, Chapter 1 (Hudson and Reed, 1979)
4	JPL Publication 81-3 (DeMore et al, 1981)
5	JPL Publication 82-57 (DeMore et al, 1982)
6	JPL Publication 83-62 (DeMore et al, 1983)
7	JPL Publication 85-37 (DeMore et al, 1985)
8	JPL Publication 87-41 (DeMore et al, 1987)

The present composition of the Panel and the major responsibilities of each member are listed below:

W. B. DeMore, Chairman (heterogeneous chemistry)

D. M. Golden (three-body reactions, equilibrium constants)

R. F. Hampson (halogen chemistry)

C. J. Howard (HO_x chemistry, $O(^1D)$ reactions, metal chemistry)

M. J. Kurylo (SO_x chemistry)

M. J. Molina (photochemical data)

A. R. Ravishankara (hydrocarbon oxidation, photochemical data)

S. P. Sander (NO_x chemistry)

As shown above, each Panel member concentrates his effort on a given area or type of data. Nevertheless, the final recommendations of the Panel represent a consensus of the entire Panel. Each member reviews the basis for all recommendations, and is cognizant of the final decision in every case. Communications regarding particular reactions may be addressed to the appropriate panel member:

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Jet Propulsion Laboratory
California Institute of Technology
Library Section, MS 111-120
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BASIS OF THE RECOMMENDATIONS

The recommended rate data and cross sections are based on laboratory measurements. In order to provide recommendations that are as up-to-date as possible, preprints and written private communications are accepted, but only when it is expected that they will appear as published journal articles. In no cases are rate constants adjusted to fit observations of stratospheric concentrations. The Panel considers the question of consistency of data with expectations based on the theory of reaction kinetics, and when a discrepancy appears to exist this fact is pointed out in the accompanying note. The major use of theoretical extrapolation of data is in connection with three-body reactions, in which the required pressure or temperature dependence is sometimes unavailable from laboratory measurements, and can be estimated by use of appropriate theoretical treatment. In the case of important rate constants for which no experimental data are available, the panel may provide estimates of rate constant parameters based on analogy to similar reactions for which data are available.

RECENT CHANGES AND CURRENT NEEDS OF LABORATORY KINETICS

There are thirty-nine changes in the rate constant recommendations in the present evaluation, but these are for the most part minor. Notable improvements have been made in the photochemistry related to Antarctic ozone depletion, as discussed in more detail in later sections. Seventy-two new reactions have been added, many of which are related to the chemistry of halocarbons. These latter compounds are being considered as possible industrial alternatives to the ozone-destroying chlorofluorocarbons, and the new reactions deal with their chemical fate in the atmosphere. As in previous evaluations, some reactions thought to be unimportant in the atmosphere are nevertheless included for completeness and for possible applications to laboratory studies. A section dealing with laboratory data on heterogeneous chemistry has been added, although this field is not yet fully amenable to evaluation. The table of enthalpy data, which was added in the last evaluation (JPL Publication 87-41), has been updated and extended.

At the time of publication of the previous evaluation, the then-recently discovered phenomenon of Antarctic ozone depletion had focussed intense interest on three areas particularly relevant to polar chemistry: (1), certain second-order reactions of halogen radicals, such as ClO + ClO and ClO + BrO; (2), heterogeneous chemistry, especially on polar strato-spheric clouds; and (3), photochemistry at temperatures below about 220 K.

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In the intervening two years, considerable progress has been made in establishing a database for gas phase (i. e., non-heterogeneous) polar photochemistry. The rates and product distributions of the ClO + ClO + M and ClO + BrO reactions have been measured more accurately, and there has been further elucidation of the chemistry and photochemistry of the ClO dimer, which is now believed to exist in the atmosphere only in the symmetric form, ClOOCl. Some important gaps remain, however, such as the identity of the photolysis products of ClOOCl. There is also the possibility that there is some missing chemistry in the photochemical model.

As mentioned in the previous evaluation, relatively few kinetics measurements have been made below about 220 K, and rate constants for this temperature regime are obtained by extrapolation of data from higher temperatures, using a simple Arrhenius expression. The accuracy of such extrapolations is somewhat questionable, however, because several key reactions seem to show non-Arrhenius behavior in this regime. Additional experiments are needed in the 200 K region to provide accurate rate data being used in the models, especially for the key reactions.

O_x Reactions

The kinetics of the O, O_2, and O_3 system are relatively well-established. However, the $O + O_2 + M$ reaction remains of fundamental importance in atmospheric chemistry. This is because the extent of ozone destruction is determined by the relative rates of competing reactions such as $O + O_3$, $O + NO_2$, $O + OH$, and $O + ClO$. Additional studies of the ozone-forming reaction, or of its relative rate compared to the competing reactions, would be useful, especially at very low temperatures.

$O(^1D)$ Reactions

The recommended rate coefficients for the $O(^1D)$ reactions correspond to the rate of removal of $O(^1D)$ which includes both chemical reactions and physical quenching of the excited O atoms. Details on the branching ratios are given in the notes.

The $O(^1D)$ reactions of 17 fluorine containing compounds have been added to this review. Most of the compounds are hydrogen containing fluorocarbons and chlorofluorocarbons that are under consideration as replacements for CFMs. These compounds are reactive toward OH radicals or are photolyzed so the $O(^1D)$ reactions will generally be a minor atmospheric loss process. On the other hand, SF_6, CF_4, and C_2F_6 do not react with OH and are not readily photolyzed so the $O(^1D)$ reactions could play an important role in their atmospheric degradation. The small amount of data available on these compounds indicates that the rate coefficients are relatively small and there is no evidence of significant chemical reaction. The data base for most of the new reactions is sparse and measurements of the rate coefficients and branching ratios would be useful.

The kinetic energy or hot atom effects of photolytically generated $O(^1D)$ are probably not important in the atmosphere, although the literature is

rich with studies of these processes and with studies of the dynamics of many $O(^1D)$ reactions. The important atmospheric reactions of $O(^1D)$ include: (1) deactivation by major gases, N_2 and O_2, which limit the $O(^1D)$ steady state concentrations; (2) reaction with trace gases, e.g., H_2O, CH_4, and N_2O, which generate radicals; and (3) reaction with long lived trace gases, e.g., HCN, which have relatively slow atmospheric degradation rates. Studies of the $O(^1D)$ reactions with HCN, CF_4, C_2F_6, and SF_6 would contribute to defining the atmospheric lifetimes of these minor species.

HO_x Reactions

There has been little change in the data base for HO_x chemistry since the last evaluation. The OH + HO_2 rate coefficient has been changed slightly to conform with recently published data. The rate coefficient for the OH + H_2O_2 reaction at 298 K is not changed although the Arrhenius parameters are revised slightly and the data set has been reevaluated to account for revisions in the H_2O_2 UV absorption cross section recommendations. The HO_2 + O_3 reaction rate coefficient remains one of the most significant uncertainties in the HO_x system. High quality data at low temperatures are needed for this key reaction.

NO_x Reactions

The changes to the data base on NO_x reactions are relatively minor. There are new entries for the reactions of OH and HO_2 with NO_3, and for the bimolecular channel of the NO_2 + NO_3 reaction. Concerning the latter reaction, a new study by Hjorth et al (1989) presented the first direct evidence for the channel giving NO + NO_2 + O_2. Whether or not this channel actually occurs is still a matter of some controversy, however. There have been some minor updates and revisions to the reactions N + O_2, N + O_3 and NO_2 + O_3.

As noted in the previous evaluation, a few of the important reactions in the NO_x family require additional work. These include the reactions which produce and remove peroxynitric acid, HO_2NO_2. Additional studies of the HO_2 + NO_2 + M recombination are needed, focusing on the temperature dependence of the low pressure limit. In addition, the temperature dependence of the important OH + HO_2NO_2 reaction is still poorly characterized. Additional work on the reactions of NH_2 radicals and subsequent oxidation steps are necessary, particularly under atmospheric conditions.

Hydrocarbon Oxidation

Our understanding of hydrocarbon oxidation in the atmosphere has improved considerably in the past decade. All hydrocarbons are released at the surface of the earth, and their degradation in the troposphere is initiated by reaction with OH (and with ozone in the case of olefins). Depending on their reactivity with OH, only a fraction of the surface flux of hydrocarbons is transported into the stratosphere, where their oxidation serves as a source of water vapor. In addition, the reaction of atomic chlorine with these hydrocarbons (mainly CH_4) constitutes one of the major

sink mechanisms for active chlorine.

In the stratosphere, CH_4 oxidation is initiated by reaction with either OH or Cl (and to a limited extent with $O(^1D)$), leading to formation of CH_3 and subsequently CH_3O_2. Some of the subsequent chemistry is not clear, primarily because the key reaction of CH_3O_2 with HO_2 is not well characterized, even though there have been new studies on this reaction. All the products of the reaction have not been identified. Some recent work suggests that, in addition to CH_3OOH, CH_2O is also formed. Our understanding of the reaction between OH and CH_3OOH has improved significantly since the last evaluation. Even though the rate constants for some of the reactions mentioned above are not well-defined, the effects of these uncertainties on stratospheric O_3 perturbation are negligible.

One area of hydrocarbon oxidation which has seen a great deal of improvement is that of product analysis. However, some additional work may be required to measure branching ratios for reactions such as CH_3O_2 + CH_3O_2 and CH_3O_2 + HO_2.

Even though CH_4 is the predominant hydrocarbon in the stratosphere, we have included in this evaluation certain reactions of a few heavier hydrocarbon species. The oxidation schemes for higher hydrocarbons have not been fully elucidated. The rates of the reactions of these hydrocarbons with OH are sufficiently well-measured to permit their rate of transport to the stratosphere to be calculated. In most cases it is expected that the radicals formed from the initial OH or Cl attack will follow courses analogous to that of CH_3, and ultimately lead to CO. However, not all the reactions involved in the conversion to CO are included. We have also added the reactions of OH with CH_3OH and C_2H_5OH.

Halogen Reactions

The kinetics database for halogen reactions shows significant expansion and improvement since the previous evaluation. It now contains rate coefficients for the reaction of OH with a large number of potential alternatives to the fully halogenated CFCs, (nine hydrochlorofluorocarbans (HCFCs) and eleven hydrofluorocarbons (HFCs)). The chemistry of these species in the troposphere is controlled by the reaction with OH in which a hydrogen atom is abstracted. There are now also upper limits for the rate constants for the reactions of OH with four brominated fully halogenated halocarbons (Halons). Other new entries include several reactions of Cl_2O_2, the dimer formed by recombination of two ClO radicals, several reactions of OClO, and reactions of NO_3 with several bromine species. The important recombination of ClO radicals to produce Cl_2O_2 has now been directly studied under polar stratospheric conditions and found to be significantly slower than had been believed on the basis of previous studies. Also the bimolecular channels have been shown to be unimportant under the same conditions. The important BrO + ClO reaction has also now been directly studied under polar stratospheric conditions. This reaction is now known to proceed through three reaction channels, and reliable temperature dependent rate expressions have been derived for the three channels. Equilibrium constants for the reactions Cl + CO $\rightarrow$ ClCO and ClO + OClO $\rightarrow$ Cl_2O_3 have been added. With these expansions

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and improvements the kinetics database for homogeneous reactions of halogen species appears to be relatively well established.

SO_x Reactions

The data base on homogeneous sulfur chemistry has seen only minor changes in the recommendations for the reactions that were included in the previous evaluation. However, this section has been expanded significantly to include many reactions that are important in the atmospheric oxidation of reduced compounds of natural and anthropogenic origin. These new entries include the reactions representing the oxidation of the radical products CH_3S and CH_3SO. There have not been significant improvements in our understanding of the oxidation of SO_2 into sulfuric acid, although there have been several direct measurements of the $HOSO_2$ intermediate. Along these same lines, further information on the reactions of SO_3 with other atmospheric species is needed to assess the competition of these reactions with SO_3 hydrolysis. Finally, further details have been provided on the mechanism for CS_2 atmospheric oxidation. The data base has also been expanded to include the reactions of NO_3 with both OCS and CS_2.

Metal Chemistry

Sodium is deposited in the upper atmosphere by meteors along with larger amounts of silicon, magnesium, and iron; comparable amounts of aluminum, nickel, and calcium; and smaller amounts of potassium, chromium, manganese, and other elements. The interest is greatest in the alkali metals because they form the least stable oxides and thus free atoms can be regenerated through photolysis and reactions with O and O_3. The other meteoric elements are expected to form more stable oxides.

The total flux of alkali metals through the atmosphere is relatively small, e.g., one or two orders of magnitude less than CFMs. Therefore extremely efficient catalytic cycles are required in order for Na to have a significant effect on stratospheric chemistry. There are no measurements of metals or metal compounds in the stratosphere which indicate a significant role.

It has been proposed that the highly polar metal compounds may polymerize to form clusters and that the stratospheric concentrations of free metal compounds are too small to play a significant role in the chemistry.

Some studies have shown that the polar species NaO and NaOH associate with abundant gases such as O_2 and CO_2 with very fast rates in the atmosphere. It has been proposed that reactions of this type will lead to the production of clusters with many molecules attached to the sodium compounds. Photolysis is expected to compete with the association reactions and to limit the cluster concentrations in daylight. If atmospheric sodium does form large clusters, it is unlikely that Na species can have a significant role in stratospheric ozone chemistry. In order to assess the importance of these processes, data are needed on the association rates and the photolysis rates involving the cluster species.

Photochemical Cross Sections

Absorption cross sections of a few important species which have highly structured absorptions are now shown graphically as well as in tabular form. These figures are only a guide, and should not be used for quantitative purposes because the measured cross sections are dependent on the resolution of the recording instrument. Figures for some haloethanes are included to show their shape.

The absorption cross sections of the Cl_2O_2 molecule formed by the association of two ClO radicals have been included. The quantum yield for the dissociation of the dimer is expected to be unity. The products of the photodissociation have not been established; however, it is assumed that Cl + ClOO are produced with unit efficiency.

The cross sections for many halocarbons which are expected to be replacements for the chlorofluoromethanes have been included. The cross sections for bromocarbons have been updated.

The temperature dependence of the absorption cross sections of species such as HO_2NO_2 and H_2O_2 in the 300 nm region may be important. We have included the measured temperature dependence for H_2O_2 in this evaluation. In the case of haloethanes and halomethanes, there are large discrepancies among the available sets of data on the magnitude of the temperature effect, and we have included only room temperature data. Further work in this area is needed.

The recommendation for the wavelength dependence of the $O(^1D)$ quantum yield in ozone photolysis has been modified to represent more closely the results obtained from laser photolysis experiments. The latter have better wavelength resolution than the earlier monochromator measurements, and thus are believed to reproduce the fall-off behavior more accurately. However, the results are not in complete agreement, particularly at the longest wavelengths, where the resolution should not be a problem. Furthermore, the temperature dependence of the $O(^1D)$ quantum yield has not been measured using the laser sources, and this should be done.

Heterogeneous Chemistry

It is now well-recognized that heterogeneous processes are crucial to stratospheric chemistry in the polar regions, and may play previously unsuspected roles in mid-latitudinal regions as well. The particle chemistry has shown a tendency to enhance the destruction of stratospheric ozone, primarily by converting inactive "reservoir" species such as HCl and $ClONO_2$ to active forms such as Cl_2 and HOCl, which are photolyzed to produce atomic chlorine and the ClO radical. Compounding the problem, the particles also appear to sequester nitrogen oxides from the stratosphere, in the form of HNO_3. Thus the normal mitigating effect of NO_x on ozone destruction by ClO_x is diminished. The net result of this chain of events is massive destruction of ozone at certain times of the year in Antarctic regions.

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The interpretation of laboratory experiments on heterogeneous chemistry is very complex and the field is still in its infancy. Experimental techniques are not as well developed as is the case for gas phase chemistry. As a consequence, we are not able to make recommendations with the confidence, reliability, and well-defined uncertainty limits that have been characteristic of the homogeneous chemistry. Nonetheless, experiments by several groups have demonstrated the apparently high efficiency of key reactions which convert chlorine reservoirs to chemically active forms. Quantitative application of the laboratory results to the stratospheric situation is difficult, however, because of uncertainties associated with the nature of the surfaces in question and other problems relating to particle microphysics and thermochemistry. These questions are discussed in somewhat more detail in the section on heterogeneous processes.

RATE CONSTANT DATA

In Table 1 (Rate Constants for Second Order Reactions) the reactions are grouped into the classes O_x, $O(^1D)$, HO_x, NO_x, Hydrocarbon Reactions, ClO_x, BrO_x, FO_x, SO_x, and metal reactions. The data in Table 2 (Rate Constants for Three-Body Reactions), while not grouped by class, are presented in the same order as the bimolecular reactions. Further, the presentation of photochemical cross section data follows the same sequence.

Bimolecular Reactions

Some of the reactions in Table 1 are actually more complex than simple two-body reactions. To explain the pressure and temperature dependences occasionally seen in reactions of this type, it is necessary to consider the bimolecular class of reactions in terms of two subcategories, direct (concerted) and indirect (non-concerted) reactions.

A direct or concerted bimolecular reaction is one in which the reactants A and B proceed to products C and D without the intermediate formation of an AB adduct which has appreciable bonding, i.e., no stable A-B molecule exists, and there is no reaction intermediate other than the transition state of the reaction, (AB)$^{\neq}$.

$$A + B \rightarrow (AB)^{\neq} \rightarrow C + D$$
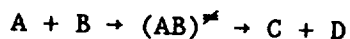
The reaction of OH with CH_4 forming $H_2O + CH_3$ is an example of a reaction of this class.

Very useful correlations between the expected structure of the transition state $[AB]^{\neq}$ and the A-factor of the reaction rate constant can be made, especially in reactions which are constrained to follow a well-defined approach of the two reactants in order to minimize energy requirements in the making and breaking of bonds. The rate constants for these reactions are well represented by the Arrhenius expression $k = A \exp(-E/RT)$ in the 200-300 K temperature range. These rate constants are not pressure dependent.

The indirect or non-concerted class of bimolecular reactions is characterized by a more complex reaction path involving a potential well between reactants and products, leading to a bound adduct (or reaction complex) formed between the reactants A and B:

$$A + B \rightleftarrows [AB]^* \rightarrow C + D$$

The intermediate $[AB]^*$ is different from the transition state $[AB]^{\neq}$, in that it is a bound molecule which can, in principle, be isolated. (Of course, transition states are involved in all of the above reactions, both forward and backward, but are not explicitly shown.) An example of this reaction type is ClO + NO, which normally produces Cl + NO_2 as a bimolecular product, but which undoubtedly involves ClONO (chlorine nitrite) as an intermediate. This can be viewed as a chemical activation process forming $(ClONO)^*$ which decomposes to the ultimate products, Cl + NO_2. Reactions of the non-concerted type can have a more complex temperature dependence, can exhibit a pressure dependence if the lifetime of $[AB]^*$ is comparable to the rate of collisional deactivation of $[AB]^*$. This arises because the relative rate at which $[AB]^*$ goes to products C + D vs. reactants A + B is a sensitive function of its excitation energy. Thus, in reactions of this type, the distinction between the bimolecular and termolecular classification becomes less meaningful, and it is especially necessary to study such reactions under the temperature and pressure conditions in which they are to be used in model calculations, or, alternatively, to develop a reliable theoretical basis for extrapolation of data.

The rate constant tabulation for second-order reactions (Table 1) is given in Arrhenius form: $k(T) = A \exp\left(\left(-\frac{E}{R}\right)\left(\frac{1}{T}\right)\right)$ and contains the following information:

1. Reaction stoichiometry and products (if known). The pressure dependences are included, where appropriate.

2. Arrhenius A-factor.

3. Temperature dependence and associated uncertainty ("activation temperature" $E/R \pm \Delta E/R$).

4. Rate constant at 298 K.

5. Uncertainty factor at 298 K.

6. Note giving basis of recommendation and any other pertinent information.

Termolecular Reactions

Rate constants for third order reactions (Table 2) of the type $A + B \underset{\leftarrow}{\rightarrow} [AB]^* \overset{M}{\rightarrow} AB$ are given in the form

$$k_o(T) = k_o^{300}(T/300)^{-n} \, cm^6 \, molecule^{-2} \, s^{-1},$$

(where k_o^{300} has been adjusted for air as the third body), together with a recommended value of n. Where pressure fall-off corrections are necessary, an additional entry gives the limiting high pressure rate constant in a similar form:

$$k_\infty(T) = k_\infty^{300}(T/300)^{-m} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

To obtain the effective second-order rate constant for a given condition of temperature and pressure (altitude), the following formula is used:

$$k(Z) = k(M,T) = \left(\frac{k_o(T)[M]}{1 + (k_o(T)[M]/k_\infty(T))}\right) 0.6^{\{1 + [\log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}$$

The fixed value 0.6 which appears in this formula fits the data for all listed reactions adequately, although in principle this quantity may be different for each reaction, and also temperature dependent.

Thus, a compilation of rate constants of this type requires the stipulation of the four parameters, $k_o(300)$, n, $k_\infty(300)$, and m. These can be found in Table 2. The discussion that follows outlines the general methods we have used in establishing this table, and the notes to the table discuss specific data sources.

Low-Pressure Limiting Rate Constant [$k_o^x(T)$]

Troe (1977) has described a simple method for obtaining low-pressure limiting rate constants. In essence this method depends on the definition:

$$k_o^x(T) = \beta_x k_{o,sc}^x(T)$$

Here sc signifies "strong" collisions, x denotes the bath gas, and β_x is an efficiency parameter ($0 < \beta < 1$), which provides a measure of energy transfer.

The coefficient β_x is related to the average energy transferred in a collision with gas x, $\langle\Delta E\rangle_x$, via:

$$\frac{\beta_x}{1-\beta_x^{1/2}} = \frac{\langle\Delta E\rangle_x}{F_E kT}$$

Notice that $\langle\Delta E\rangle$ is quite sensitive to β. F_E is the correction factor of the energy dependence of the density of states (a quantity of the order of 1.1 for most species of stratospheric interest).

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For many of the reactions of possible stratospheric interest reviewed here, there exist data in the low-pressure limit (or very close thereto), and we have chosen to evaluate and unify this data by calculating $k_{o,sc}^x(T)$ for the appropriate bath gas x and computing the value of β_x corresponding to the experimental value [Troe (1977)]. A compilation (Patrick and Golden, 1983) gives details for many of the reactions considered here.

From the β_x values (most of which are for N_2, i.e., β_{N2}), we compute $<\Delta E>_x$ according to the above equation. Values of $<\Delta E>_{N2}$ of approximately 0.3-1 kcal $mole^{-1}$ are generally expected. If multiple data exist, we average the values of $<\Delta E>_{N2}$ and recommend a rate constant corresponding to the β_{N2} computed in the equation above.

Where no data exist we have estimated the low-pressure rate constant by taking β_{N2} = 0.3 at T = 300 K, a value based on those cases where data exist.

Temperature Dependence of Low-Pressure Limiting Rate Constants: n

The value of n recommended here comes from measurements or, in some cases, a calculation of $<\Delta E>_{N2}$ from the data at 300 K, and a computation of β_{N2} (200 K) assuming that $<\Delta E>_{N2}$ is independent of temperature in this range. This β_{N2} (200 K) value is combined with the computed value of k_o^{sc} (200 K) to give the expected value of the actual rate constant at 200 K. This latter in combination with the value at 300 K yields the value of n.

This procedure can be directly compared with measured values of k_o (200 K) when those exist. Unfortunately, very few values at 200 K are available. There are often temperature-dependent studies, but some ambiguity exists when one attempts to extrapolate these down to 200 K. If data are to be extrapolated beyond the measured temperature range, a choice must be made as to the functional form of the temperature dependence. There are two general ways of expressing the temperature dependence of rate constants. Either the Arrhenius expression $k_o(T) = A\exp(-E/RT)$ or the form $k_o(T) = A' T^{-n}$ is employed. Since neither of these extrapolation techniques is soundly based, and since they often yield values that differ substantially, we have used the method explained earlier as the basis of our recommendations.

High-Pressure Limit Rate Constants [$k_\infty(T)$]

High-pressure rate constants can often be obtained experimentally, but those for the relatively small species of atmospheric importance usually reach the high-pressure limit at inaccessibly high pressures. This leaves two sources of these numbers, the first being guesses based upon some model, and the second being extrapolation of fall-off data up to higher pressures. Stratospheric conditions generally render reactions of interest much closer to the low-pressure limit, and thus are fairly insensitive to the high-pressure value. This means that while the extrapolation is long, and the value of $k_\infty(T)$ not very accurate, a "reasonable guess" of $k_\infty(T)$ will then suffice. In some cases we have declined to guess since the low-pressure limit is effective over the entire range of stratospheric conditions.

Temperature Dependence of High-Pressure Limit Rate Constants: m

There are very little data upon which to base a recommendation for values of m. Values in Table 2 are estimated, based on models for the transition state of bond association reactions and whatever data are available.

Isomer Formation

A particular problem with association reactions arises when there are easily accessible isomeric forms of the molecule AB. In this situation, if the laboratory measurement of the rate constant is accomplished by following the disappearance of reactants, the value ascertained may be the sum of two or more processes that should be measured and tabulated independently. A specific example of such a case is found in Table 2 for the reactions of Cl-atoms with NO_2. These reactants may come together to form either $ClNO_2$ or ClONO. Whether or not isomer formation, such as discussed above, is important depends on the relative stability of the possible products. At the moment the only case that we are sure about is the above example. In the past however, there was some thought that data on the reaction between ClO radicals and NO_2 could be understood only in terms of the formation of both chlorine nitrate ($ClONO_2$) and other isomers (ClOONO, OClONO). Experiments have shown that this is not the case and that chlorine nitrate is the sole product. This question is discussed at some length in note 16 of Table 2.

There are many other possibilities for isomer formation in the reactions listed in Table 2. In some of the notes we have specifically pointed this out, but even for reactions where no mention is made of isomers, because we felt that they could not contribute under atmospheric conditions, extrapolation to higher pressures and lower temperatures should be done with the possibilities kept in mind.

Uncertainty Estimates

For second-order rate constants in Table 1, an estimate of the uncertainty at any given temperature may be obtained from the following expression:

$$f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$$

An upper or lower bound (corresponding approximately to one standard deviation) of the rate constant at any temperature T can be obtained by multiplying or dividing the value of the rate constant at that temperature by the factor f(T). The quantities f(298) and $\Delta E/R$ are, respectively, the uncertainty in the rate constant at 298 K and in the Arrhenius temperature coefficient, as listed in Table 1. This approach is based on the fact that rate constants are almost always known with minimum uncertainty at room temperature. The overall uncertainty normally increases at other temperatures, because there are usually fewer data and it is almost always more difficult to make measurements at other temperatures. It is important to note that the

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uncertainty at a temperature T <u>cannot</u> be calculated from the expression $\exp(\Delta E/RT)$. The above expression for $f(T)$ must be used to obtain the correct result.

The uncertainty represented by $f(T)$ is normally symmetric; i.e., the rate constant may be greater than or less than the central value, $k(T)$, by the factor $f(T)$. In a few cases in Table 1 asymmetric uncertainties are given in the temperature coefficient. For these cases, the factors by which a rate constant are to be multiplied or divided to obtain, respectively, the upper and lower limits are not equal, except at 298 K where the factor is simply $f(298 \text{ K})$. Explicit equations are given below for the case where the temperature dependence is (E/R +a, -b):

For T > 298 K, multiply by the factor

$$f(298 \text{ K})e^{[a(1/298-1/T)]}$$

and divide by the factor

$$f(298 \text{ K})e^{[b(1/298-1/T)]}$$

For T < 298 K, multiply by the factor

$$f(298 \text{ K})e^{[b(1/T-1/298)]}$$

and divide by the factor

$$f(298 \text{ K})e^{[a(1/T-1/298)]}$$

Examples of symmetric and asymmetric error limits are shown in Figure 1.

For three-body reactions (Table 2) a somewhat analogous procedure is used. Uncertainties expressed as increments to k_o and k_∞ are given for these rate constants at room temperature. The additional uncertainty arising from the temperature extrapolation is expressed as an uncertainty in the temperature coefficients n and m.

The assigned uncertainties represent the subjective judgment of the Panel. They are not determined by a rigorous, statistical analysis of the data base, which generally is too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experiments, and the potential for systematic errors. There is obviously no way to quantify these "unknown" errors. The spread in results among different techniques for a given reaction may provide some basis for an uncertainty, but the possibility of the same, or compensating, systematic errors in all the studies must be recognized. Furthermore, the probability distribution may not follow the normal, Gaussian form. For measurements subject to large systematic errors, the true rate constant may be much further from the recommended value than would be expected based on a Gaussian distribution with the stated uncertainty. As an example, the recommended rate constants for the reactions HO_2 + NO and Cl + $ClONO_2$ have changed by factors of 30-50, occurrences which could not have been allowed for with any reasonable values of σ in a Gaussian distribution.

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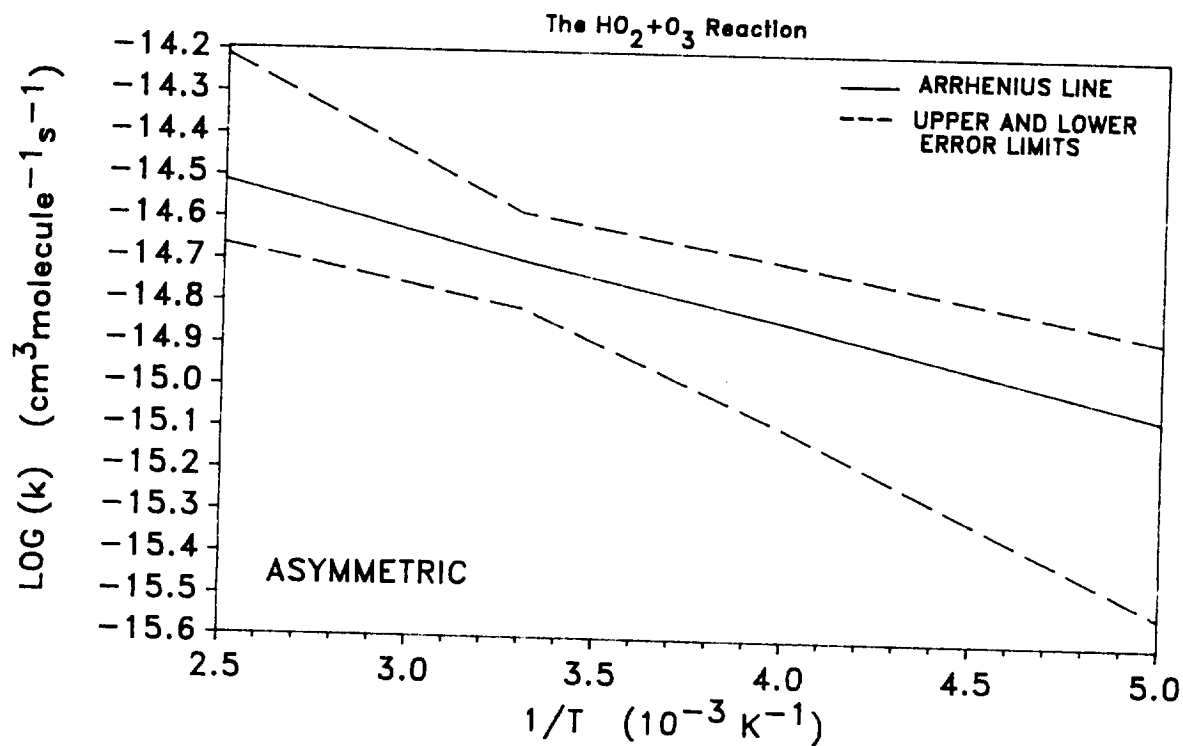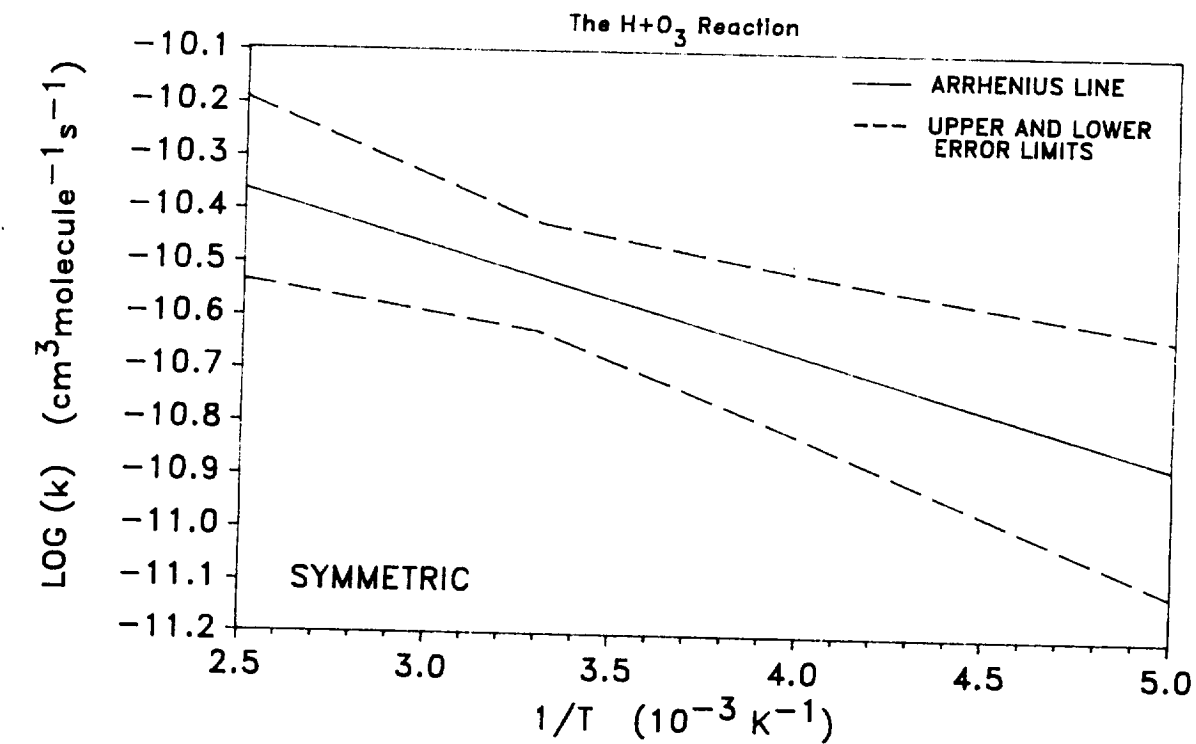
Figure 1.   Symmetric and Asymmetric Error Limits

Units

The rate constants are given in units of concentration expressed as molecules per cubic centimeter and time in seconds. Thus, for first-, second-, and third-order reactions the units of k are s^{-1}, cm^3 molecule^{-1} s^{-1}, and cm^6 molecule^{-2} s^{-1}, respectively. Cross sections are expressed as cm^2 molecule^{-1}, base e.

Table 1. Rate Constants for Second Order Reactions[a]

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
O_x Reactions					
$O + O_2 \xrightarrow{M} O_3$	(See Table 2)				
$O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060 ± 250	8.0×10^{-15}	1.15	A1
$O(^1D)$ Reactions					
& $O(^1D) + N_2O \rightarrow N_2 + O_2$	4.9×10^{-11}	0 ± 100	4.9×10^{-11}	1.3	A2, A3
$\rightarrow NO + NO$	6.7×10^{-11}	0 ± 100	6.7×10^{-11}	1.3	A2, A3
$O(^1D) + H_2O \rightarrow OH + OH$	2.2×10^{-10}	0 ± 100	2.2×10^{-10}	1.2	A2, A4
$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.4×10^{-10}	0 ± 100	1.4×10^{-10}	1.2	A2, A5
$\rightarrow H_2 + CH_2O$	1.4×10^{-11}	0 ± 100	1.4×10^{-11}	1.2	A2, A5
& $O(^1D) + H_2 \rightarrow OH + H$	1.0×10^{-10}	0 ± 100	1.0×10^{-10}	1.2	A2, A6
$O(^1D) + N_2 \rightarrow O + N_2$	1.8×10^{-11}	$-(110 \pm 100)$	2.6×10^{-11}	1.2	A2
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(See Table 2)				
$O(^1D) + O_2 \rightarrow O + O_2$	3.2×10^{-11}	$-(70 \pm 100)$	4.0×10^{-11}	1.2	A2
$O(^1D) + CO_2 \rightarrow O + CO_2$	7.4×10^{-11}	$-(120 \pm 100)$	1.1×10^{-10}	1.2	A2
$O(^1D) + O_3 \rightarrow O_2 + O_2$	1.2×10^{-10}	0 ± 100	1.2×10^{-10}	1.3	A2, A7
$\rightarrow O_2 + O + O$	1.2×10^{-10}	0 ± 100	1.2×10^{-10}	1.3	A2, A7
$O(^1D) + HCl \rightarrow products$	1.5×10^{-10}	0 ± 100	1.5×10^{-10}	1.2	A8
$O(^1D) + HF \rightarrow OH + F$	1.4×10^{-10}	0 ± 100	1.4×10^{-10}	2.0	A9
$O(^1D) + HBr \rightarrow products$	1.5×10^{-10}	0 ± 100	1.5×10^{-10}	2.0	A10
$O(^1D) + Cl_2 \rightarrow products$	2.8×10^{-10}	0 ± 100	2.8×10^{-10}	2.0	A11

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

\# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$O(^1D) + CCl_4 \rightarrow$ products	3.3×10^{-10}	0 ± 100	3.3×10^{-10}	1.2	A2, A12
$O(^1D) + CFCl_3 \rightarrow$ products	2.3×10^{-10}	0 ± 100	2.3×10^{-10}	1.2	A2, A12
$O(^1D) + CF_2Cl_2 \rightarrow$ products	1.4×10^{-10}	0 ± 100	1.4×10^{-10}	1.3	A2, A12
* $O(^1D) + CF_4 \rightarrow CF_4 + O$	-	-	$<1.8 \times 10^{-13}$	-	A2, A13
$O(^1D) + CCl_2O \rightarrow$ products	3.6×10^{-10}	0 ± 100	3.6×10^{-10}	2.0	A2, A14
$O(^1D) + CFClO \rightarrow$ products	1.9×10^{-10}	0 ± 100	1.9×10^{-10}	2.0	A2, A14
$O(^1D) + CF_2O \rightarrow$ products	7.4×10^{-11}	0 ± 100	7.4×10^{-11}	2.0	A2, A14
$O(^1D) + NH_3 \rightarrow OH + NH_2$	2.5×10^{-10}	0 ± 100	2.5×10^{-10}	1.3	A2, A15
# $O(^1D) + CHFCl_2 \rightarrow$ products	1.9×10^{-10}	0 ± 100	1.9×10^{-10}	1.3	A16, A12
# $O(^1D) + CHF_2Cl \rightarrow$ products	9.5×10^{-11}	0 ± 100	9.5×10^{-11}	1.3	A17, A12
# $O(^1D) + CHF_3 \rightarrow$ products	8.4×10^{-12}	0 ± 100	8.4×10^{-12}	5.0	A18, A12
# $O(^1D) + CH_2F_2 \rightarrow$ products	9×10^{-11}	0 ± 100	9×10^{-11}	3.0	A19, A12
# $O(^1D) + CH_3F \rightarrow$ products	1.4×10^{-10}	0 ± 100	1.4×10^{-10}	2.0	A20, A12
# $O(^1D) + CHCl_2CF_3 \rightarrow$ products	2.2×10^{-10}	0 ± 100	2.2×10^{-10}	2.0	A21, A12
# $O(^1D) + CHFClCF_3 \rightarrow$ products	1×10^{-10}	0 ± 100	1×10^{-10}	3.0	A22, A12
# $O(^1D) + CHF_2CF_3 \rightarrow$ products	5×10^{-11}	0 ± 100	5×10^{-11}	5.0	A23, A12
# $O(^1D) + CH_2ClCF_2Cl \rightarrow$ products	1.6×10^{-10}	0 ± 100	1.6×10^{-10}	2.0	A24, A12
# $O(^1D) + CH_2ClCF_3 \rightarrow$ products	1.5×10^{-10}	0 ± 100	1.5×10^{-10}	2.0	A25, A12
# $O(^1D) + CH_2FCF_3 \rightarrow$ products	1×10^{-10}	0 ± 100	1×10^{-10}	3.0	A26, A12
# $O(^1D) + CH_3CFCl_2 \rightarrow$ products	1.5×10^{-10}	0 ± 100	1.5×10^{-10}	3.0	A27, A12
# $O(^1D) + CH_3CF_2Cl \rightarrow$ products	1.4×10^{-10}	0 ± 100	1.4×10^{-10}	2.0	A28, A12

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
# O(^{1}D) + CH$_3$CF$_3$ → products	1.0×10^{-10}	0±100	1.0×10^{-10}	3.0	A29, A12
# O(^{1}D) + CH$_3$CHF$_2$ → products	1×10^{-10}	0±100	1×10^{-10}	5.0	A30, A12
# O(^{1}D) + C$_2$F$_6$ → O + C$_2$F$_6$	-	-	$<2 \times 10^{-13}$	-	A31
# O(^{1}D) + SF$_6$ → products	-	-	$<4.5 \times 10^{-14}$	-	A32

HO$_x$ Reactions

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
H + O$_2$ $\xrightarrow{M}$ HO$_2$	(See Table 2)				
H + O$_3$ → OH + O$_2$	1.4×10^{-10}	470±200	2.9×10^{-11}	1.25	B1
& H + HO$_2$ → products	8.1×10^{-11}	0±200	8.1×10^{-11}	1.3	B2
O + OH → O$_2$ + H	2.2×10^{-11}	-(120±100)	3.3×10^{-11}	1.2	B3
O + HO$_2$ → OH + O$_2$	3.0×10^{-11}	-(200±100)	5.9×10^{-11}	1.2	B4
O + H$_2$O$_2$ → OH + HO$_2$	1.4×10^{-12}	2000±1000	1.7×10^{-15}	2.0	B5
* OH + HO$_2$ → H$_2$O + O$_2$	4.8×10^{-11}	-(250±200)	1.1×10^{-10}	1.3	B6
OH + O$_3$ → HO$_2$ + O$_2$	1.6×10^{-12}	940±300	6.8×10^{-14}	1.3	B7
OH + OH → H$_2$O + O	4.2×10^{-12}	240±240	1.9×10^{-12}	1.4	B8
$\xrightarrow{M}$ H$_2$O$_2$	(See Table 2)				
* OH + H$_2$O$_2$ → H$_2$O + HO$_2$	2.8×10^{-12}	160±100	1.7×10^{-12}	1.2	B9
OH + H$_2$ → H$_2$O + H	5.5×10^{-12}	2000±400	6.7×10^{-15}	1.2	B10
& HO$_2$ + HO$_2$ → H$_2$O$_2$ + O$_2$	2.3×10^{-13}	-(600±200)	1.7×10^{-12}	1.3	B11
$\xrightarrow{M}$ H$_2$O$_2$ + O$_2$	1.7×10^{-33}[M]	-(1000±400)	4.9×10^{-32}[M]	1.3	B11
& HO$_2$ + O$_3$ → OH + 2O$_2$	1.1×10^{-14}	500$^{+500}_{-100}$	2.0×10^{-15}	1.3	B12

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp\left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

NO_x Reactions

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
* $N + O_2 \rightarrow NO + O$	1.5×10^{-11}	3600±400	8.5×10^{-17}	1.25	C1
* $N + O_3 \rightarrow NO + O_2$	-	-	$< 2.0 \times 10^{-16}$	-	C2
$N + NO \rightarrow N_2 + O$	3.4×10^{-11}	0±100	3.4×10^{-11}	1.3	C3
$N + NO_2 \rightarrow N_2O + O$	-	-	3.0×10^{-12}	3.0	C4
$O + NO \overset{M}{\rightarrow} NO_2$	(See Table 2)				
$O + NO_2 \rightarrow NO + O_2$	6.5×10^{-12}	-(120±120)	9.7×10^{-12}	1.1	C5
$O + NO_2 \overset{M}{\rightarrow} NO_3$	(See Table 2)				
$O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0±150	1.0×10^{-11}	1.5	C6
$O + N_2O_5 \rightarrow$ products	-	-	$< 3.0 \times 10^{-16}$	-	C7
$O + HNO_3 \rightarrow OH + NO_3$	-	-	$< 3.0 \times 10^{-17}$	-	C8
$O + HO_2NO_2 \rightarrow$ products	7.8×10^{-11}	3400±750	8.6×10^{-16}	3.0	C9
$O_3 + NO \rightarrow NO_2 + O_2$	2.0×10^{-12}	1400±200	1.8×10^{-14}	1.2	C10
$NO + HO_2 \rightarrow NO_2 + OH$	3.7×10^{-12}	-(240±80)	8.3×10^{-12}	1.2	C11
$NO + NO_3 \rightarrow 2NO_2$	1.7×10^{-11}	-(150±100)	2.9×10^{-11}	1.3	C12
$OH + NO \overset{M}{\rightarrow} HONO$	(See Table 2)				
$OH + NO_2 \overset{M}{\rightarrow} HNO_3$	(See Table 2)				
# $OH + NO_3 \rightarrow$ products	-	-	2.3×10^{-11}	2.0	C13
$OH + HNO_3 \rightarrow H_2O + NO_3$	(See Note C13 and ≠ below)			1.3	C14

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

≠ $OH + HNO_3$ pressure and temperature dependence fit by

$$k(M,T) = k_o + \frac{k_3[M]}{1 + \dfrac{k_3[M]}{k_2}} \quad \text{with} \quad \begin{cases} k_o = 7.2 \times 10^{-15} \exp(785/T) \\ k_2 = 4.1 \times 10^{-16} \exp(1440/T) \\ k_3 = 1.9 \times 10^{-33} \exp(725/T) \end{cases}$$

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$OH + HO_2NO_2 \rightarrow$ products	1.3×10^{-12}	$-(380^{+270}_{-500})$	4.6×10^{-12}	1.5	C15
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 2)				
# $HO_2 + NO_3 \rightarrow$ products	-	-	4.1×10^{-12}	2.0	C16
* $O_3 + NO_2 \rightarrow NO_3 + O_2$	1.2×10^{-13}	2450 ± 150	3.2×10^{-17}	1.15	C17
$O_3 + HNO_2 \rightarrow O_2 + HNO_3$	-	-	$<5.0 \times 10^{-19}$	-	C18
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(See Table 2)				
# $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	(See Note)				C19
& $N_2O_5 + H_2O \rightarrow 2HNO_3$	-	-	$<2.0 \times 10^{-21}$	-	C20
$OH + NH_3 \rightarrow H_2O + NH_2$	3.6×10^{-12}	930 ± 200	1.6×10^{-13}	1.4	C21
$NH_2 + HO_2 \rightarrow$ products	-	-	3.4×10^{-11}	2.0	C22
$NH_2 + NO \rightarrow$ products	3.8×10^{-12}	$-(450 \pm 150)$	1.7×10^{-11}	2.0	C23
$NH_2 + NO_2 \rightarrow$ products	2.1×10^{-12}	$-(650 \pm 250)$	1.9×10^{-11}	3.0	C24
$NH_2 + O_2 \rightarrow$ products	-	-	$<3.0 \times 10^{-18}$	-	C25
* $NH_2 + O_3 \rightarrow$ products	4.3×10^{-12}	930 ± 500	1.9×10^{-13}	3.0	C26

Hydrocarbon Reactions

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$OH + CO \rightarrow CO_2 + H$	$1.5 \times 10^{-13}(1+0.6P_{atm})$	0 ± 300	$1.5 \times 10^{-13}(1+0.6P_{atm})$	1.3	D1
& $OH + CH_4 \rightarrow CH_3 + H_2O$	2.3×10^{-12}	1700 ± 200	7.7×10^{-15}	1.2	D2
$OH + {}^{13}CH_4 \rightarrow {}^{13}CH_3 + H_2O$	(See Note)				D3
& $OH + C_2H_6 \rightarrow H_2O + C_2H_5$	1.1×10^{-11}	1100 ± 200	2.8×10^{-13}	1.2	D4
$OH + C_3H_8 \rightarrow H_2O + C_3H_7$	1.4×10^{-11}	750 ± 200	1.1×10^{-12}	1.3	D5

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp\left|\frac{\Delta E}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
OH + C_2H_4 → products	(See Table 2)				
OH + C_2H_2 → products	(See Table 2)				
& OH + H_2CO → H_2O + HCO	1.0×10^{-11}	0±200	1.0×10^{-11}	1.25	D6
# OH + CH_3OH → products	6.7×10^{-12}	600±300	8.9×10^{-13}	1.2	D7
# OH + C_2H_5OH → products	6.8×10^{-12}	225±100	3.2×10^{-12}	1.3	D8
OH + CH_3CHO → CH_3CO + H_2O	6.0×10^{-12}	-(250±200)	1.4×10^{-11}	1.4	D9
* OH + CH_3OOH → products	3.8×10^{-12}	-(200±200)	7.4×10^{-12}	1.5	D10
OH + HCN → products	1.2×10^{-13}	400±150	3.1×10^{-14}	3.0	D11
OH + CH_3CN → products	4.5×10^{-13}	900±400	2.2×10^{-14}	2.0	D12
# O_3 + C_2H_2 → products	1.0×10^{-14}	4100±500	1.0×10^{-20}	3.0	D13
# O_3 + C_2H_4 → products	1.2×10^{-14}	2630±100	1.7×10^{-18}	1.25	D14
# O_3 + C_3H_6 → products	6.5×10^{-15}	1900±200	1.1×10^{-17}	1.2	D15
* HO_2 + CH_2O → adduct	6.7×10^{-15}	-(600±600)	5.0×10^{-14}	5.0	D16
O + HCN → products	1.0×10^{-11}	4000±1000	1.5×10^{-17}	10.0	D17
O + C_2H_2 → products	3.0×10^{-11}	1600±250	1.4×10^{-13}	1.3	D18
O + H_2CO → products	3.4×10^{-11}	1600±250	1.6×10^{-13}	1.25	D19
O + CH_3CHO → CH_3CO + OH	1.8×10^{-11}	1100±200	4.5×10^{-13}	1.25	D20
O + CH_3 → products	1.1×10^{-10}	0±250	1.1×10^{-10}	1.3	D21
& CH_3 + O_2 → products	-	-	$<3.0 \times 10^{-16}$	-	D22
CH_3 + O_2 $\xrightarrow{M}$ CH_3O_2	(See Table 2)				
# C_2H_5 + O_2 → C_2H_4 + HO_2	-	-	$<2.0 \times 10^{-15}$	-	D23

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2$	(See Table 2)				
* $CH_2OH + O_2 \rightarrow CH_2O + HO_2$	(See Note)		9.1×10^{-12}	1.3	D24
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	3.9×10^{-14}	900±300	1.9×10^{-15}	1.5	D25
$HCO + O_2 \rightarrow CO + HO_2$	3.5×10^{-12}	-(140±140)	5.5×10^{-12}	1.3	D26
$CH_3 + O_3 \rightarrow$ products	5.4×10^{-12}	220±150	2.6×10^{-12}	2.0	D27
$CH_3O_2 + O_3 \rightarrow$ products	-	-	$<3.0 \times 10^{-17}$	-	D28
* $CH_3O_2 + CH_3O_2 \rightarrow$ products	2.2×10^{-13}	-(220±220)	4.6×10^{-13}	1.5	D29
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	4.2×10^{-12}	-(180±180)	7.6×10^{-12}	1.2	D30
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(See Table 2)				
* $CH_3O_2 + HO_2 \rightarrow$ products	3.3×10^{-13}	-(800±400)	4.8×10^{-12}	2.0	D31
# $C_2H_5O_2 + C_2H_5O_2 \rightarrow$ products	1.6×10^{-13}	300±250	5.8×10^{-14}	2.0	D32
# $C_2H_5O_2 + NO \rightarrow$ products	8.9×10^{-12}	0±300	8.9×10^{-12}	1.3	D33
# $C_2H_5O_2 + HO_2 \rightarrow$ products	6.5×10^{-13}	-(650±300)	5.8×10^{-12}	2.0	D34
$NO_3 + CO \rightarrow$ products	-	-	$<4.0 \times 10^{-19}$	-	D35
* $NO_3 + CH_2O \rightarrow$ products	-	-	5.8×10^{-16}	1.3	D36
$NO_3 + CH_3CHO \rightarrow$ products	1.4×10^{-12}	1900±300	2.4×10^{-15}	1.3	D37

<u>ClO_x Reactions</u>

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
& $Cl + O_3 \rightarrow ClO + O_2$	2.9×10^{-11}	260±100	1.2×10^{-11}	1.15	E1
$Cl + H_2 \rightarrow HCl + H$	3.7×10^{-11}	2300±200	1.6×10^{-14}	1.25	E2
& $Cl + CH_4 \rightarrow HCl + CH_3$	1.1×10^{-11}	1400±150	1.0×10^{-13}	1.1	E3

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
Cl + C_2H_6 → HCl + C_2H_5	7.7×10^{-11}	90±90	5.7×10^{-11}	1.1	E4
& Cl + C_3H_8 → HCl + C_3H_7	1.4×10^{-10}	-(40±250)	1.6×10^{-10}	1.5	E5
Cl + C_2H_2 → products	(See Table 2)				
& Cl + CH_3OH → CH_2OH + HCl	5.7×10^{-11}	0±250	5.7×10^{-11}	1.5	E6
Cl + CH_3Cl → CH_2Cl + HCl	3.3×10^{-11}	1250±200	4.9×10^{-13}	1.2	E7
Cl + CH_3CN → products	-	-	$<2.0 \times 10^{-15}$	-	E8
Cl + CH_3CCl_3 → CH_2CCl_3 + HCl	-	-	$<4.0 \times 10^{-14}$	-	E9
Cl + H_2CO → HCl + HCO	8.1×10^{-11}	30±100	7.3×10^{-11}	1.15	E10
Cl + H_2O_2 → HCl + HO_2	1.1×10^{-11}	980±500	4.1×10^{-13}	1.5	E11
Cl + HOCl → Cl_2 + OH	3.0×10^{-12}	130±250	1.9×10^{-12}	2.0	E12
* Cl + HNO_3 → products	-	-	$<2.0 \times 10^{-16}$	-	E13
Cl + HO_2 → HCl + O_2	1.8×10^{-11}	-(170±200)	3.2×10^{-11}	1.5	E14
→ OH + ClO	4.1×10^{-11}	450±200	9.1×10^{-12}	2.0	E14
Cl + Cl_2O → Cl_2 + ClO	9.8×10^{-11}	0±250	9.8×10^{-11}	1.2	E15
* Cl + OClO → ClO + ClO	3.4×10^{-11}	-(160±200)	5.8×10^{-11}	1.25	E16
Cl + ClOO → Cl_2 + O_2	1.4×10^{-10}	0±250	1.4×10^{-10}	3.0	E17
→ ClO + ClO	8.0×10^{-12}	0±250	8.0×10^{-12}	3.0	E17
# Cl + Cl_2O_2 → products	-	-	1.0×10^{-10}	2.0	E18
Cl + $ClONO_2$ → products	6.8×10^{-12}	-(160±200)	1.2×10^{-11}	1.3	E19
Cl + NO $\xrightarrow{M}$ NOCl	(See Table 2)				
Cl + NO_2 $\xrightarrow{M}$ ClONO ($ClNO_2$)	(See Table 2)				

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
* Cl + NO$_3$ → ClO + NO$_2$	2.6×10^{-11}	0±400	2.6×10^{-11}	2.0	E20
Cl + N$_2$O → ClO + N$_2$	(See Note)				E21
* Cl + ClNO → NO + Cl$_2$	5.8×10^{-11}	-(100±200)	8.1×10^{-11}	1.5	E22
Cl + O$_2$ $\xrightarrow{M}$ ClOO	(See Table 2)				
& ClO + O → Cl + O$_2$	3.0×10^{-11}	-(70±70)	3.8×10^{-11}	1.2	E23
ClO + NO → NO$_2$ + Cl	6.4×10^{-12}	-(290±100)	1.7×10^{-11}	1.15	E24
ClO + NO$_2$ $\xrightarrow{M}$ ClONO$_2$	(See Table 2)				
ClO + NO$_3$ → products	4.0×10^{-13}	0±400	4.0×10^{-13}	2.0	E25
ClO + HO$_2$ → HOCl + O$_2$	4.8×10^{-13}	-(700±$^{250}_{700}$)	5.0×10^{-12}	1.4	E26
ClO + H$_2$CO → products	~1.0×10^{-12}	>2100	<1.0×10^{-15}	-	E27
ClO + OH → products	1.1×10^{-11}	-(120±150)	1.7×10^{-11}	1.5	E28
ClO + CH$_4$ → products	~1.0×10^{-12}	>3700	<4.0×10^{-18}	-	E29
ClO + H$_2$ → products	~1.0×10^{-12}	>4800	<1.0×10^{-19}	-	E29
ClO + CO → products	~1.0×10^{-12}	>3700	<4.0×10^{-18}	-	E29
ClO + N$_2$O → products	~1.0×10^{-12}	>4300	<6.0×10^{-19}	-	E29
ClO + ClO → products	8.0×10^{-13}	1250±500	1.2×10^{-14}	2.0	E30
$\xrightarrow{M}$ Cl$_2$O$_2$	(See Table 2)				
ClO + O$_3$ → ClOO + O$_2$	1.0×10^{-12}	>4000	<1.0×10^{-18}	-	E31
→ OClO + O$_2$	1.0×10^{-12}	>4000	<1.0×10^{-18}	-	E31
# ClO + CH$_3$O$_2$ → products	(See Note)				E32
OH + Cl$_2$ → HOCl + Cl	1.4×10^{-12}	900±400	6.7×10^{-14}	1.2	E33

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
OH + HCl → H$_2$O + Cl	2.6x10^{-12}	350±100	8.0x10^{-13}	1.3	E34
OH + HOCl → H$_2$O + ClO	3.0x10^{-12}	500±500	5.0x10^{-13}	3.0	E35
* OH + CH$_3$Cl → CH$_2$Cl + H$_2$O	2.1x10^{-12}	1150±200	4.4x10^{-14}	1.2	E36
* OH + CH$_2$Cl$_2$ → CHCl$_2$ + H$_2$O	5.8x10^{-12}	1100±250	1.4x10^{-13}	1.2	E37
* OH + CHCl$_3$ → CCl$_3$ + H$_2$O	4.3x10^{-12}	1100±200	1.1x10^{-13}	1.2	E38
* OH + CHFCl$_2$ → CFCl$_2$ + H$_2$O	1.2x10^{-12}	1100±150	3.0x10^{-14}	1.1	E39
* OH + CHF$_2$Cl → CF$_2$Cl + H$_2$O	1.2x10^{-12}	1650±150	4.7x10^{-15}	1.1	E40
* OH + CH$_2$ClF → CHClF + H$_2$O	3.0x10^{-12}	1250±200	4.5x10^{-14}	1.15	E41
OH + CH$_3$CCl$_3$ → CH$_2$CCl$_3$ + H$_2$O	5.0x10^{-12}	1800±200	1.2x10^{-14}	1.3	E42
* OH + CHCl$_2$CF$_3$ → CCl$_2$CF$_3$ + H$_2$O	6.4x10^{-13}	850±250	3.7x10^{-14}	1.2	E43
* OH + CHFClCF$_3$ → CFClCF$_3$ + H$_2$O	6.6x10^{-13}	1250±300	1.0x10^{-14}	1.2	E44
* OH + CH$_2$ClCF$_2$Cl → CHClCF$_2$Cl + H$_2$O	3.6x10^{-12}	1600±400	1.7x10^{-14}	2.0	E45
# OH + CH$_2$ClCF$_3$ → CHClCF$_3$ + H$_2$O	5.2x10^{-13}	1100±300	1.3x10^{-14}	1.3	E46
* OH + CH$_3$CFCl$_2$ → CH$_2$CFCl$_2$ + H$_2$O	4.2x10^{-13}	1200±300	7.5x10^{-15}	1.3	E47
* OH + CH$_3$CF$_2$Cl → CH$_2$CF$_2$Cl + H$_2$O	9.6x10^{-13}	1650±250	3.8x10^{-15}	1.2	E48
OH + C$_2$Cl$_4$ → products	9.4x10^{-12}	1200±200	1.7x10^{-13}	1.25	E49
OH + C$_2$HCl$_3$ → products	4.9x10^{-13}	-(450±200)	2.2x10^{-12}	1.25	E50
# OH + CCl$_4$ → products	~1.0x10^{-12}	>2300	<5.0x10^{-16}	-	E51
OH + CFCl$_3$ → products	~1.0x10^{-12}	>3700	<5.0x10^{-18}	-	E52
OH + CF$_2$Cl$_2$ → products	~1.0x10^{-12}	>3600	<6.0x10^{-18}	-	E52
OH + ClONO$_2$ → products	1.2x10^{-12}	330±200	3.9x10^{-13}	1.5	E53

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp\left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
O + HCl → OH + Cl	1.0×10^{-11}	3300±350	1.5×10^{-16}	2.0	E54
O + HOCl → OH + ClO	1.0×10^{-11}	2200±1000	6.0×10^{-15}	10.0	E55
O + ClONO$_2$ → products	2.9×10^{-12}	800±200	2.0×10^{-13}	1.5	E56
O + Cl$_2$O → ClO + ClO	2.9×10^{-11}	630±200	3.5×10^{-12}	1.4	E57
OClO + O → ClO + O$_2$	2.8×10^{-11}	1200±300	5.0×10^{-13}	2.0	E58
# OClO + O$_3$ → products	2.1×10^{-12}	4700±1000	3.0×10^{-19}	2.5	E59
# OClO + OH → HOCl + O$_2$	4.5×10^{-13}	-(800±200)	6.8×10^{-12}	2.0	E60
OClO + NO → NO$_2$ + ClO	2.5×10^{-12}	600±300	3.4×10^{-13}	2.0	E61
# Cl$_2$O$_2$ + O$_3$ → products	-	-	$<1.0 \times 10^{-19}$	-	E62
# Cl$_2$O$_2$ + NO → products	-	-	$<2.0 \times 10^{-14}$	-	E63
# HCl + NO$_3$ → HNO$_3$ + Cl	-	-	$<5.0 \times 10^{-17}$	-	E64
HCl + ClONO$_2$ → products	-	-	$<1.0 \times 10^{-20}$	-	E65
* HCl + HO$_2$NO$_2$ → products	-	-	$<1.0 \times 10^{-21}$	-	E66
H$_2$O + ClONO$_2$ → products	-	-	$<2.0 \times 10^{-21}$	-	E67
CF$_2$ClO$_2$ + NO → CF$_2$ClO + NO$_2$	3.1×10^{-12}	-(500±200)	1.6×10^{-11}	1.3	E68
CFCl$_2$O$_2$ + NO → CFCl$_2$O + NO$_2$	3.5×10^{-12}	-(430±200)	1.5×10^{-11}	1.3	E68
CCl$_3$O$_2$ + NO → CCl$_3$O + NO$_2$	5.7×10^{-12}	-(330±200)	1.7×10^{-11}	1.3	E68

BrO$_x$ Reactions

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
& Br + O$_3$ → BrO + O$_2$	1.7×10^{-11}	800±200	1.2×10^{-12}	1.2	F1
Br + H$_2$O$_2$ → HBr + HO$_2$	1.0×10^{-11}	>3000	$<5.0 \times 10^{-16}$	-	F2

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
Br + H₂CO → HBr + HCO	1.7×10^{-11}	800±200	1.1×10^{-12}	1.3	F3
& Br + HO₂ → HBr + O₂	1.5×10^{-11}	600±600	2.0×10^{-12}	2.0	F4
* Br + Cl₂O → BrCl + ClO	2.0×10^{-11}	500±300	3.8×10^{-12}	2.0	F5
# Br + OClO → BrO + ClO	2.6×10^{-11}	1300±300	3.4×10^{-13}	2.0	F6
# Br + Cl₂O₂ → products	-	-	3.0×10^{-12}	2.0	F7
BrO + O → Br + O₂	3.0×10^{-11}	0±250	3.0×10^{-11}	3.0	F8
* BrO + ClO → Br + OClO	1.6×10^{-12}	-(430±200)	6.8×10^{-12}	1.25	F9
→ Br + ClOO	2.9×10^{-12}	-(220±200)	6.1×10^{-12}	1.25	F9
→ BrCl + O₂	5.8×10^{-13}	-(170±200)	1.0×10^{-12}	1.25	F9
BrO + NO → NO₂ + Br	8.8×10^{-12}	-(260±130)	2.1×10^{-11}	1.15	F10
BrO + NO₂ →ᴹ BrONO₂	(See Table 2)				
BrO + BrO → 2 Br + O₂	1.4×10^{-12}	-(150±150)	2.3×10^{-12}	1.25	F11
→ Br₂ + O₂	6.0×10^{-14}	-(600±600)	4.4×10^{-13}	1.25	F11
BrO + O₃ → Br + 2O₂	~1.0×10^{-12}	>1600	<5.0×10^{-15}	-	F12
BrO + HO₂ → products	-	-	5.0×10^{-12}	3.0	F13
BrO + OH → products	-	-	1.0×10^{-11}	5.0	F14
OH + Br₂ → HOBr + Br	4.2×10^{-11}	0±600	4.2×10^{-11}	1.3	F15
OH + HBr → H₂O + Br	1.1×10^{-11}	0±250	1.1×10^{-11}	1.2	F16
* OH + CH₃Br → CH₂Br + H₂O	6.8×10^{-13}	850±200	3.8×10^{-14}	1.25	F17
# OH + CF₂Br₂ → products	-	-	<5.0×10^{-16}	-	F18
# OH + CF₂ClBr → products	-	-	<1.5×10^{-16}	-	F18

[a] Units are cm³/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
# OH + CF_3Br → products	-	-	$<1.2x10^{-16}$	-	F18
# OH + CF_2BrCF_2Br → products	-	-	$<1.5x10^{-16}$	-	F18
* O + HBr → OH + Br	$5.8x10^{-12}$	1500±200	$3.8x10^{-14}$	1.3	F19
# NO_3 + Br → BrO + NO_2	-	-	$1.6x10^{-11}$	2.0	F20
# NO_3 + BrO → products	-	-	$1.0x10^{-12}$	3.0	F20
# NO_3 + HBr → HNO_3 + Br	-	-	$<1.0x10^{-16}$	-	F20

FO_x Reactions

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
F + O_3 → FO + O_2	$2.8x10^{-11}$	230±200	$1.3x10^{-11}$	2.0	G1
* F + H_2 → HF + H	$1.4x10^{-10}$	500±200	$2.6x10^{-11}$	1.2	G2
F + CH_4 → HF + CH_3	$3.0x10^{-10}$	400±300	$8.0x10^{-11}$	1.5	G3
* F + H_2O → HF + OH	$1.4x10^{-11}$	0±200	$1.4x10^{-11}$	1.3	G4
F + O_2 $\xrightarrow{M}$ FO_2	(See Table 2)				
F + NO $\xrightarrow{M}$ FNO	(See Table 2)				
F + NO_2 $\xrightarrow{M}$ FNO_2(FONO)	(See Table 2)				
# F + HNO_3 → HF + NO_3	$6.0x10^{-12}$	-(400±200)	$2.3x10^{-11}$	1.3	G5
NO + FO → NO_2 + F	$2.6x10^{-11}$	0±250	$2.6x10^{-11}$	2.0	G6
FO + FO → 2 F + O_2	$1.5x10^{-11}$	0±250	$1.5x10^{-11}$	3.0	G7
FO + O_3 → F + 2 O_2	(See Note)				G8
→ FO_2 + O_2	(See Note)				G8
FO + NO_2 $\xrightarrow{M}$ $FONO_2$	(See Table 2)				

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp\left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
O + FO → F + O$_2$	5.0×10^{-11}	0±250	5.0×10^{-11}	3.0	G9
O + FO$_2$ → FO + O$_2$	5.0×10^{-11}	0±250	5.0×10^{-11}	5.0	G10
# OH + CHF$_3$ → CF$_3$ + H$_2$O	1.5×10^{-12}	2650±500	2.1×10^{-16}	1.5	G11
# OH + CH$_2$F$_2$ → CHF$_2$ + H$_2$O	2.5×10^{-12}	1650±200	1.0×10^{-14}	1.2	G12
# OH + CH$_3$F → CH$_2$F + H$_2$O	5.4×10^{-12}	1700±300	1.8×10^{-14}	1.2	G13
# OH + CHF$_2$CF$_3$ → CF$_2$CF$_3$ + H$_2$O	8.9×10^{-13}	1750±500	2.5×10^{-15}	2.0	G14
# OH + CHF$_2$CHF$_2$ → CF$_2$CHF$_2$ + H$_2$O	8.7×10^{-13}	1500±500	5.7×10^{-15}	2.0	G15
* OH + CH$_2$FCF$_3$ → CHFCF$_3$ + H$_2$O	1.7×10^{-12}	1750±300	4.8×10^{-15}	1.2	G16
# OH + CH$_2$FCHF$_2$ → products	2.8×10^{-12}	1500±500	1.8×10^{-14}	2.0	G17
# OH + CH$_3$CF$_3$ → CH$_2$CF$_3$ + H$_2$O	6.0×10^{-13}	1750±500	1.7×10^{-15}	2.0	G18
# OH + CH$_2$FCH$_2$F → CHFCH$_2$F + H$_2$O	1.7×10^{-11}	1500±500	1.1×10^{-13}	2.0	G19
* OH + CH$_3$CHF$_2$ → products	1.5×10^{-12}	1100±200	3.7×10^{-14}	1.1	G20
# OH + CH$_3$CH$_2$F → products	1.3×10^{-11}	1200±300	2.3×10^{-13}	2.0	G21
CF$_3$O$_2$ + NO → CF$_3$O + NO$_2$	3.9×10^{-12}	-(400±200)	1.5×10^{-11}	1.3	G22

SO$_x$ Reactions

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
* OH + H$_2$S → SH + H$_2$O	6.0×10^{-12}	75±75	4.7×10^{-12}	1.2	H1
OH + OCS → products	1.1×10^{-13}	1200±500	1.9×10^{-15}	2.0	H2
& OH + CS$_2$ → products	(See Note)	-	-	-	H3
OH + SO$_2$ $\xrightarrow{M}$ HOSO$_2$	(See Table 2)				
O + H$_2$S → OH + SH	9.2×10^{-12}	1800±550	2.2×10^{-14}	1.7	H4

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[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp\left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
O + OCS → CO + SO	2.1×10^{-11}	2200±150	1.3×10^{-14}	1.2	H5
O + CS$_2$ → CS + SO	3.2×10^{-11}	650±150	3.6×10^{-12}	1.2	H6
S + O$_2$ → SO + O	2.3×10^{-12}	0±200	2.3×10^{-12}	1.2	H7
S + O$_3$ → SO + O$_2$	-	-	1.2×10^{-11}	2.0	H8
S + OH → SO + H	-	-	6.6×10^{-11}	3.0	H9
SO + O$_2$ → SO$_2$ + O	2.6×10^{-13}	2400±500	8.4×10^{-17}	2.0	H10
SO + O$_3$ → SO$_2$ + O$_2$	3.6×10^{-12}	1100±200	9.0×10^{-14}	1.2	H11
SO + OH → SO$_2$ + H	-	-	8.6×10^{-11}	2.0	H12
SO + NO$_2$ → SO$_2$ + NO	1.4×10^{-11}	0±50	1.4×10^{-11}	1.2	H13
SO + ClO → SO$_2$ + Cl	2.8×10^{-11}	0±50	2.8×10^{-11}	1.3	H14
SO + OClO → SO$_2$ + ClO	-	-	1.9×10^{-12}	3.0	H15
SO + BrO → SO$_2$ + Br	-	-	5.7×10^{-11}	1.4	H16
SO$_2$ + HO$_2$ → products	-	-	$<1.0 \times 10^{-18}$	-	H17
SO$_2$ + CH$_3$O$_2$ → products	-	-	$<5.0 \times 10^{-17}$	-	H18
SO$_2$ + NO$_2$ → products	-	-	$<2.0 \times 10^{-26}$	-	H19
SO$_3$ + NO$_2$ → products	-	-	1.0×10^{-19}	10.0	H19
& SO$_2$ + NO$_3$ → products	-	-	$<7.0 \times 10^{-21}$	-	H20
SO$_2$ + O$_3$ → SO$_3$ + O$_2$	3.0×10^{-12}	>7000	$<2.0 \times 10^{-22}$	-	H21
# SO$_3$ + H$_2$O → H$_2$SO$_4$	-	-	$<6.0 \times 10^{-15}$	-	H22
Cl + H$_2$S → HCl + SH	5.7×10^{-11}	0±50	5.7×10^{-11}	1.3	H23
Cl + OCS → SCl + CO	-	-	$<1.0 \times 10^{-16}$	-	H24

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
ClO + OCS → products	-	-	$<2.0 \times 10^{-16}$	-	H25
ClO + SO_2 → Cl + SO_3	-	-	$<4.0 \times 10^{-18}$	-	H25
SH + H_2O_2 → products	-	-	$<5.0 \times 10^{-15}$	-	H26
SH + O → H + SO	-	-	1.6×10^{-10}	5.0	H27
SH + O_2 → OH + SO	-	-	$<4.0 \times 10^{-19}$	-	H28
* SH + O_3 → HSO + O_2	9.0×10^{-12}	280±200	3.5×10^{-12}	1.3	H29
& SH + NO_2 → HSO + NO	2.9×10^{-11}	-(240±100)	6.5×10^{-11}	1.3	H30
SH + NO $\xrightarrow{M}$ HSNO	(See Table 2)				
HSO + NO → products	-	-	$<1.0 \times 10^{-15}$	-	H31
HSO + NO_2 → HSO₂ + NO	-	-	9.6×10^{-12}	2.0	H31
HSO + O_2 → products	-	-	$<2.0 \times 10^{-17}$	-	H31
HSO + O_3 → products	-	-	1.0×10^{-13}	5.0	H32
HSO_2 + O_2 → HO_2 + SO_2	-	-	3.0×10^{-13}	3.0	H33
& $HOSO_2$ + O_2 → HO_2 + SO_3	1.3×10^{-12}	330±200	4.4×10^{-13}	1.2	H34
* H_2S + NO_3 → products	-	-	$<8.0 \times 10^{-16}$	-	H35
CS + O_2 → OCS + O	-	-	2.9×10^{-19}	2.0	H36
CS + O_3 → OCS + O_2	-	-	3.0×10^{-16}	3.0	H37
CS + NO_2 → OCS + NO	-	-	7.6×10^{-17}	3.0	H37
# OH + CH_3SH → products	9.9×10^{-12}	-(360±100)	3.3×10^{-11}	1.2	H38
# OH + CH_3SCH_3 → H_2O + CH_2SCH_3	1.1×10^{-11}	240±100	4.9×10^{-12}	1.2	H39.
# OH + CH_3SSCH_3 → products	5.7×10^{-11}	-(380±300)	2.0×10^{-10}	1.3	H40

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
# NO_3 + CH_3SH → products	4.4×10^{-13}	-(210±210)	8.9×10^{-13}	1.25	H41
# NO_3 + CH_3SCH_3 → products	1.9×10^{-13}	-(500±200)	1.0×10^{-12}	1.2	H42
# NO_3 + CH_3SSCH_3 → products	1.3×10^{-12}	270±270	5.3×10^{-13}	1.4	H43
# NO_3 + CS_2 → products	-	-	$<4.0 \times 10^{-16}$	-	H44
# NO_3 + OCS → products	-	-	$<3.0 \times 10^{-15}$	-	H45
# CH_3S + O_2 → products	-	-	$<3.0 \times 10^{-18}$	-	H46
# CH_3S + O_3 → products	-	-	4.1×10^{-12}	2.0	H47
# CH_3S + NO_2 → products	-	-	5.6×10^{-11}	1.3	H48
# CH_3SO + O_3 → products	-	-	1.0×10^{-12}	3.0	H49
# CH_3SO + NO_2 → CH_3SO_2 + NO	-	-	1.2×10^{-11}	1.4	H50

Metal Reactions

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
Na + O_2 $\xrightarrow{M}$ NaO_2	(See Table 2)				
* Na + O_3 → NaO + O_2	7.6×10^{-10}	0±400	7.6×10^{-10}	1.2	J1
→ NaO_2 + O	$<4 \times 10^{-11}$	0±400	$<4.0 \times 10^{-11}$	-	J1
& Na + N_2O → NaO + N_2	2.4×10^{-10}	1600±400	1.1×10^{-12}	1.3	J2
Na + Cl_2 → NaCl + Cl	7.3×10^{-10}	0±200	7.3×10^{-10}	1.3	J3
NaO + O → Na + O_2	3.7×10^{-10}	0±400	3.7×10^{-10}	3.0	J4
NaO + O_2 $\xrightarrow{M}$ NaO_3	(See Table 2)				
NaO + O_3 → NaO_2 + O_2	1.6×10^{-10}	0±400	1.6×10^{-10}	2.0	J5
→ Na + $2O_2$	6×10^{-11}	0±800	6.0×10^{-11}	3.0	J5

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
NaO + H$_2$ → NaOH + H	2.6×10^{-11}	0±600	2.6×10^{-11}	2.0	J6
NaO + H$_2$O → NaOH + OH	2.2×10^{-10}	0±400	2.2×10^{-10}	2.0	J7
NaO + NO → Na + NO$_2$	1.5×10^{-10}	0±400	1.5×10^{-10}	4.0	J8
NaO + CO$_2$ $\xrightarrow{M}$ NaCO$_3$	(See Table 2)				
NaO + HCl → products	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J9
NaO$_2$ + NO → NaO + NO$_2$			$<10^{-14}$		J10
NaO$_2$ + HCl → products	2.3×10^{-10}	0±400	2.3×10^{-10}	3.0	J11
NaOH + HCl → NaCl + H$_2$O	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J12
NaOH + CO$_2$ $\xrightarrow{M}$ NaHCO$_3$	(See Table 2)				

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty factor at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 87-41).

# Indicates a new entry that was not in the previous evaluation.

& Indicates a change in the Note.

NOTES TO TABLE 1

A1. $O + O_3$. The recommended rate expression is from Wine et al (1983) and is a linear least squares fit of all data (unweighted) from Davis et al (1973b), McCrumb and Kaufman (1972), West et al (1978), Arnold and Comes (1979), and Wine et al (1983).

A2. $O(^1D)$ Reactions. These recommendations are based on averages of the absolute rate constant measurements reported by Streit et al (1976), Davidson et al (1977) and Davidson et al (1978) for N_2O, H_2O, CH_4, H_2, N_2, O_2, O_3, CCl_4, $CFCl_3$, CF_2Cl_2, NH_3, and CO_2; by Amimoto et al (1978), Amimoto et al (1979), and Force and Wiesenfeld (1981a,b) for N_2O, H_2O, CH_4, N_2, H_2, O_2, O_3, CO_2, CCl_4, $CFCl_3$, CF_2Cl_2, and CF_4; by Wine and Ravishankara (1981, 1982, 1983) for N_2O, H_2O, N_2, H_2, O_3, CO_2, and CF_2O; by Brock and Watson (private communication, 1980) for N_2, O_2 and CO_2; by Lee and Slanger (1978 and 1979) for H_2O and O_2; and by Gericke and Comes (1981) for H_2. The weight of the evidence from these studies indicates that the results of Heidner and Husain (1973), Heidner et al (1973) and Fletcher and Husain (1976a, 1976b) contain a systematic error. For the critical atmospheric reactants, such as N_2O, H_2O, and CH_4, the recommended absolute rate constants are in good agreement with the previous relative measurements when compared with N_2 as the reference reactant. A similar comparison with O_2 as the reference reactant gives somewhat poorer agreement.

A3. $O(^1D) + N_2O$. The branching ratio for the reaction of $O(^1D)$ with N_2O to give $N_2 + O_2$ or $NO + NO$ is an average of the values reported by Davidson et al (1979); Volltrauer et al (1979); Marx et al (1979) and Lam et al (1981), with a spread in $k(NO + NO)/k(TOTAL) = 0.52 - 0.62$. The recommended branching ratio agrees well with earlier measurements of the quantum yield from N_2O photolysis (Calvert and Pitts 1966b). The $O(^1D)$ translational energy and temperature dependence effects are not clearly resolved. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + N_2O$ is <4.0%. The uncertainty for this reaction includes factors for both the overall rate coefficient and the branching ratio. A direct measurement by Greenblatt and Ravishankara (1989) of the NO yield from the $O(^1D) + N_2O$ reaction in the presence of air-like mixtures agrees very well with the value predicted using the recommended $O(^1D)$ rate constants for N_2, O_2, and N_2O and the $O(^1D) + N_2O$ product branching ratio. These authors suggest that their results support the recommendations and reduce the uncertainty in the collected rate parameters by over a factor of two.

A4. $O(^1D) + H_2O$. Measurements of the $O_2 + H_2$ product yield were made by Zellner et al (1980) (1+0.5 or -1)% and by Glinski and Birks (1985) (0.006 + 0.007 or -0.006)%. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + H_2O$ is <(4.9±3.2)%.

A5. $O(^1D) + CH_4$. The branching ratio for the reaction of $O(^1D)$ with CH_4 to give $OH + CH_3$ or $CH_2O + H_2$ is from Lin and DeMore (1973). A molecular beam study by Casavecchia et al (1980) indicates that an additional path forming CH_3O (or CH_2OH) + H may be important. This possibility requires further investigation. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + CH_4$ is <4.3%.

A6. $O(^1D) + H_2$. Wine and Ravishankara (1982) have determined the yield of $O(^3P)$ is < 4.9%. The major products are H + OH.

A7. $O(^1D) + O_3$. The branching ratio for reaction of $O(^1D)$ with O_3 to give $O_2 + O_2$ or $O_2 + O + O$ is from Davenport et al (1972). This is supported by measurements of Amimoto et al (1978) who reported that on average one ground state O is produced per $O(^1D)$ reaction with O_3. It seems unlikely that this could result from 100% quenching of the $O(^1D)$ by O_3.

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A8. $O(^1D)$ + HCl. The recommendation is the average of measurements by Davidson et al, (1977) and Wine et al (1986). Product studies by the latter indicate: $O(^3P)$ + HCl(9±5)%; H + ClO(24±5)%; and OH + Cl(67±10)%.

A9. $O(^1D)$ + HF. Rate coefficient and product yield measured by Wine et al (1984, private communication). The $O(^3P)$ yield is less than 4%.

A10. $O(^1D)$ + HBr. Rate coefficient and products measured by Wine et al (1986). Product yields: HBr + $O(^3P)$ (20±7)%, H + BrO <4.5%, and OH + Br (80±12)%.

A11. $O(^1D)$ + Cl_2. Rate coefficient and $O(^3P)$ product measured by Wine et al (1985). Product yields: Cl_2 + $O(^3P)$ (25±10)%. The balance is probably ClO + Cl. An earlier indirect study by Freudenstein and Biedenkapp (1976) is in reasonable agreement on the yield of ClO.

A12. $O(^1D)$ + halocarbons. The halocarbon rate constants are for the total disappearance of $O(^1D)$ and probably include physical quenching. Products of the reactive channels may include CX_3O + X, CX_2O + X_2, and CX_3 + XO, where X = H, F, or Cl in various combinations. Chlorine and hydrogen are more easily displaced than fluorine from halocarbons. Some values have been reported for the fractions of the total rate of disappearance of $O(^1D)$ proceeding through physical quenching and reactive channels. For CCl_4: quenching = (14±6)% and reaction = (86±6)%, (Force and Wiesenfeld, 1981a); for $CFCl_3$: quenching = (25±10)%, ClO formation = (60±15)% (Donovan, private communication, 1980); for CF_2Cl_2: quenching = (14±7)% and reaction = (86±14)% (Force and Wiesenfeld, 1981a), quenching = (20±10)%, ClO formation = (55±15)% (Donovan, private communication, 1980).

A13. $O(^1D)$ + CF_4. The recommendation is based upon measurements by Force and Wiesenfeld (1981a). It is given as an upper limit because the reported rate coefficient can be accounted for by physical quenching by a 0.4% impurity in the CF_4 reactant.

A14. $O(^1D)$ + CCl_2O, CFClO and CF_2O. For the reactions of $O(^1D)$ with CCl_2O and CFClO the recommended rate constants are derived from data of Fletcher and Husain (1978). For consistency, the recommended values for these rate constants were derived using a scaling factor (0.5) which corrects for the difference between rate constants from the Husain Laboratory and the recommendations for other $O(^1D)$ rate constants in this table. The recommendation for CF_2O is from the data of Wine and Ravishankara (1983). Their result is preferred over the value of Fletcher and Husain (1978) because it appears to follow the pattern of decreased reactivity with increased fluorine substitution observed for other halocarbons. These reactions have been studied only at 298 K. Based on consideration of similar $O(^1D)$ reactions, it is assumed that E/R equals zero, and therefore the value shown for the A-factor has been set equal to k(298 K).

A15. $O(^1D)$ + NH_3. Sanders et al (1980a) have detected the products $NH(a^1\Delta)$ and OH formed in the reaction. They report the yield of $NH(a^1\Delta)$ is in the range 3-15% of the amount of OH detected.

A16. $O(^1D)$ + $CHFCl_2$. New Entry. The recommendation is based upon the measurement by Davidson et al (1978) of the total rate coefficient (physical quenching and reaction).

A17. $O(^1D)$ + CHF_2Cl. New Entry. The recommendation is based upon the measurement by Davidson et al (1978) of the total rate coefficient. A measurement of the rate of reaction (halocarbon removal) relative to the rate of reaction with N_2O by Green and Wayne (1976/77a) agrees very well with this value when the $O(^1D)$ + N_2O recommendation is used to obtain an absolute value. A relative measurement by Atkinson et al (1976) gives a rate coefficient about a factor of two higher. Addison et al (1979) reported the following product yields: ClO 55 ± 10%, CF_2 45 ± 10%, $O(^3P)$ 28 +10 or -15%, and OH 5%, where the $O(^3P)$ comes from a branch yielding CF_2 and HCl. It appears that chemical reaction predominates.

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A18. $O(^1D)$ + CHF_3. New Entry. The recommendation is based upon the measurement of Force and Wiesenfeld (1981) who also reported that the rate coefficient is partitioned between physical quenching (77%) and reactive loss of CHF_3 (23%). The recommendation has a large error limit because it seems inconsistent with the recommended value for the analogous compound CHF_2CF_3.

A19. $O(^1D)$ + CH_2F_2. New Entry. The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_2F_2 relative to the loss of N_2O. The recommendation for N_2O is used to obtain an estimated rate coefficient for reactive loss of CH_2F_2, 4.6×10^{-11}. This has been increased by a factor of two to obtain the recommendation based on the assumption that physical quenching will account for about 50% of the total $O(^1D)$ loss. This estimate is made by analogy to the data for CHF_3 and CH_3F from Force and Wiesenfeld (1981).

A20. $O(^1D)$ + CH_3F. New Entry. The recommendation is based upon the measurement of Force and Wiesenfeld (1981) who also reported that the rate coefficient is partitioned between physical quenching (25%) and reactive loss of CH_3F (75%).

A21. $O(^1D)$ + $CHCl_2CF_3$. New Entry. The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of $CHCl_2CF_3$ relative to the loss of N_2O. The recommendation for N_2O is used to obtain the value given. Some physical quenching probably occurs. The recommended value for the analogous compound CHF_3.

A22. $O(^1D)$ + $CHClFCF_3$. New Entry. There are no data on this reaction. The recommendation is an estimate based on analogy to similar compounds.

A23. $O(^1D)$ + CHF_2CF_3. New Entry. The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CHF_2CF_3 relative to the los of N_2O. The recommendation for N_2O is used to obtain the value given. Some physical quenching probably occurs. The recommendation has a large error limit because it seems inconsistent with the recommended value for the analogous compound CHF_3.

A24. $O(^1D)$ + CH_2ClCF_2Cl. New Entry. The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_2ClCF_2Cl relative to the loss of N_2O. The recommendation for N_2O is used to obtain the value given. It is assumed that there is no physical quenching.

A25. $O(^1D)$ + CH_2ClCF_3. New Entry. The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_2ClCF_3 relative to the loss of N_2O. The recommendation for N_2O is used to obtain the value given. It is assumed that there is no physical quenching.

A26. $O(^1D)$ + CH_2FCF_3. New Entry. There are no data on this reaction. The recommendation is an estimate based on analogy to similar compounds, particularly CH_2F_2. There may be significant physical quenching for this compound.

A27. $O(^1D)$ + CH_3CFCl_2. New Entry. The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_3CFCl_2 relative to the loss of N_2O. The recommendation for N_2O is used to obtain the value given. It is assumed that there is no physical quenching.

A28. $O(^1D)$ + CH_3CF_2Cl. New Entry. The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_3CF_2Cl relative to the loss of N_2O. The recommendation for N_2O is used to obtain the value given. It is assumed that there is no physical quenching.

A29. $O(^1D)$ + CH_3CF_3. New Entry. The recommendation is based upon the relative rate measurement of Green and Wayne (1976/77a) who measured the loss of CH_3CF_3 relative to the loss of N_2O. The recommendation for N_2O is used to obtain the value given. It is assumed that there is no physical quenching.

A30. $O(^1D)$ + CH_3CHF_2. New Entry. There are no data on this reaction. The recommendation is an estimate based on analogy to similar compounds, particularly CH_3CF_3 and CH_3F. There may be significant physical quenching for this compound.

A31. $O(^1D)$ + C_2F_6. New Entry. There are no data on this reaction. The recommendation is based on analogy to CF_4.

A32. $O(^1D)$ + SF_6. New Entry. The upper limit value is derived from data in Fig. 2a of Davidson et al (1976). The observed first-order decay was assumed to be due to $O(^1D)$ removal by SF_6 and O_3. The amount due to reaction with O_3 was calculated and subtracted from the total first-order decay rate coefficient. The residual decay was attributed to removal by SF_6, although it includes some contribution from trace and impurity gases such as O_2 from the O_3 source. The true rate coefficient may be much smaller than the recommendation. Any reaction that occurs is likely to be physical quenching.

B1. H + O_3. The recommendation is an average of the recent results of Lee et al (1978b) and Keyser (1979), which are in excellent agreement over the 200-400 K range. An earlier study by Clyne and Monkhouse (1977) is in very good agreement on the T dependence in the range 300-560 K but lies about 60% below the recommended values. Although we have no reason not to believe the Clyne and Monkhouse values, we prefer the two studies that are in excellent agreement, especially since they were carried out over the T range of interest. Recent results by Finlayson-Pitts and Kleindienst (1979) agree well with the present recommendations. Reports of a channel forming HO_2 + O (Finlayson-Pitts and Kleindienst, 1979: ~25%, and Force and Wiesenfeld, 1981b: ~40%) have been contradicted by other studies (Howard and Finlayson-Pitts, 1980: <3%; Washida et al, 1980a: <6%; Finlayson-Pitts et al, 1981: <2%); and Dodonov et al, 1985: <0.3%). Secondary chemistry is believed to be responsible for the observed O-atoms in this system. Washida et al (1980c) measured a low limit (<0.1%) for the production of singlet molecular oxygen in the reaction H + O_3.

B2. H + HO_2. There are five recent studies of this reaction: Hack et al (1978), Hack et al (1979c), Thrush and Wilkinson (1981b), Sridharan et al (1982) and Keyser (1986). Related early work and combustion studies are referenced in the Sridharan et al paper. All five studies used discharge flow systems. It is difficult to obtain a direct measurement of the rate constant for this reaction because both reactants are radicals and the products OH and O are very reactive toward the HO_2 reactant. The recommendation is based on the data of Sridharan et al and Keyser because their measurements were the most direct and required the fewest corrections. The other measurements, (5.0 ± 1.3) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} by Thrush and Wilkinson (1981b) and (4.65 ± 1) x 10^{-11} by Hack et al (1979c) are in reasonable agreement with the recommended value. Three of the studies reported the product channels: (a) 2OH, (b) H_2O + O, and (c) H_2 + O_2. Hack et al (1978) k_a/k = 0.69, $k_b/k \leq 0.02$, and k_c/k = 0.29; Sridharan et al (1982) k_a/k = 0.87±0.04, k_b/k = 0.04±0.02, k_c/k = 0.09±.045; and Keyser (1986) k_a/k = 0.90±0.04, k_b/k = 0.02±0.02, and k_c/k = 0.08±0.04. Hislop and Wayne (1977), Keyser et al (1985), and Michelangeli et al (1988) reported on the yield of $O_2(b^1\Sigma)$ formed in channel (c) as (2.8 ± 1.3) x 10^{-4}, <8 x 10^{-3}, and <2.1 x 10^{-2} respectively of the total reactions. Keyser found the rate coefficient and product yields to be independent of temperature for 245 < T < 300 K.

B3. O + OH. The rate constant for O + OH is a fit to three temperature dependence studies: Westenberg et al (1970a), Lewis and Watson (1980), Howard and Smith (1981). This recommendation is consistent with earlier work near room temperature as reviewed by Lewis and Watson (1980) and with the recent

measurements of Brune et al (1983). The ratio k(O + HO$_2$)/k(O + OH) measured by Keyser (1983) agrees with the rate constants recommended here.

B4.   O + HO$_2$. The recommendation for the O + HO$_2$ reaction rate constant is the average of five studies at room temperature (Keyser, 1982, Sridharan et al, 1982, Ravishankara et al, 1983b, Brune et al, 1983 and Nicovich and Wine, 1987) fitted to the temperature dependence given by Keyser (1982) and Nicovich and Wine (1987). Earlier studies by Hack et al (1979a) and Burrows et al (1977, 1979) are not considered, because the OH + H$_2$O$_2$ reaction was important in these studies and the value used for its rate constant in their analyses has been shown to be in error. Data from Lii et al (1980c) is not considered, because it is based on only four experiments and involves a curve fitting procedure that appears to be insensitive to the desired rate constant. Data from Ravishankara et al (1983b) at 298 K show no dependence on pressure between 10 and 500 torr N$_2$. The ratio k(O + HO$_2$)/k(O + OH) measured by Keyser (1983) agrees with the rate constants recommended here. Sridharan et al (1985) showed that the reaction products correspond to abstraction of an oxygen atom from HO$_2$ by the O reactant. Keyser et al (1985) reported <1% O$_2$ (b$^1\Sigma$) yield.

B5.   O + H$_2$O$_2$. There are two direct studies of the O + H$_2$O$_2$ reaction: Davis et al (1974c) and Wine et al (1983). The recommended value is a fit to the combined data. Wine et al suggest that the earlier measurements may be too high because of secondary chemistry. The A-factor for both data sets is quite low compared to similar atom-molecule reactions. An indirect measurement of the E/R by Roscoe (1982) is consistent with the recommendation.

B6.   OH + HO$_2$. A study by Keyser (1988) appears to resolve a discrepancy between low pressure discharge flow experiments which all gave rate coefficients near 7 x 10^{-11} cm^3 molecule^{-1} s^{-1}: Keyser (1981), Thrush and Wilkinson (1981a), Sridharan et al (1981, 1984), Temps and Wagner (1982), and Rozenshtein et al (1984), and atmospheric pressure studies which gave rate coefficients near 11 x 10^{-11}: Lii et al (1980a), Hochanadel et al (1980), DeMore (1982), Cox et al (1981), Burrows et al (1981) and Kurylo et al (1981). Laboratory measurements using a discharge flow experiment and a chemical model analysis of the results by Keyser (1988) demonstrate that the previous discharge flow measurements were probably subject to interference from small amounts of O and H. In the presence of excess HO$_2$ these atoms generate OH and result in a rate coefficient measurement which falls below the true value. The temperature dependence is from Keyser (1988) who covered the range 254 to 382 K. A flow tube study by Schwab et al (1989) reported k = (8.0 $^{+3}_{-4}$) x 10^{-11} in agreement with the recommendation. These workers measured the concentrations of HO$_2$, OH, O, and H and used a computer model of the relevant reactions to test for interference. A flow tube study by Dransfeld and Wagner (1986) employing isotope labelled ^{18}OH reactant obtained k = (11 ± 2) x 10^{-11} in good agreement with the recommendation. They attributed about half of the reactive events to isotope scrambling because control experiments with ^{16}OH gave k = 6 x 10^{-11}. It should be noted that their control experiments were subject to the errors described by Keyser (1988) due to the presence of small amounts of H and O whereas their ^{18}OH measurements were not. Kurylo et al (1981) found no evidence of significant scrambling in isotope studies of the OH and HO$_2$ reaction. An additional careful study of the reaction temperature dependence would be useful.

B7.   OH + O$_3$. The recommendation for the OH + O$_3$ rate constant is based on the room temperature measurements of Kurylo (1973) and Zahniser and Howard (1980) and the temperature dependence studies of Anderson and Kaufman (1973), Ravishankara et al (1979b) and Smith et al (1984). Kurylo's value was adjusted (-8%) to correct for an error in the ozone concentration measurement (Hampson and Garvin, 1977). The Anderson and Kaufman rate constants were normalized to k = 6.2 x 10^{-14} cm^3 molecule^{-1} s^{-1} at 295 K as suggested by Chang and Kaufman (1978).

B8.   OH + OH. The recommendation for the OH + OH reaction is the average of six measurements near 298 K: Westenberg and de Haas (1973a), McKenzie et al (1973), Clyne and Down (1974), Trainor and von Rosenberg (1974), Farquharson and Smith (1980) and Wagner and Zellner (1981). The rate constants

for these studies all fall between (1.4 and 2.3) x 10^{-12} cm^3 molecule^{-1} s^{-1}. The temperature dependence is from Wagner and Zellner, who reported rate constants for the range T = 250-580 K.

B9. OH + H$_2$O$_2$. The recommendation is a fit to the temperature dependence studies of Keyser (1980b), Sridharan et al (1980), Wine et al (1981c), Kurylo et al (1982b), and Vaghjiani et al (1989). The data from these studies have been revised to account for the H$_2$O$_2$ UV absorption cross section recommendations in this evaluation. The first two references contain a discussion of some possible reasons for the discrepancies with earlier work and an assessment of the impact of the new value on other kinetic studies. All of these measurements agree quite well and overlap one another. Measurements by Lamb et al (1983) agree at room temperature but indicate a quite different temperature dependence with k increasing slightly with decreasing temperature. Their data were not incorporated in the fit. A measurement at room temperature by Marinelli and Johnston (1982a) agrees well with the recommendation.

B10. OH + H$_2$. The OH + H$_2$ reaction has been the subject of numerous studies (see Ravishankara et al (1981b) for a review of experimental and theoretical work). The recommendation is fixed to the average of nine studies at 298 K: Greiner (1969), Stuhl and Niki (1972), Westenberg and de Haas (1973c), Smith and Zellner (1974), Atkinson et al. (1975), Overend et al (1975), Tully and Ravishankara (1980), Zellner and Steinert (1981), and Ravishankara et al (1981b).

B11. HO$_2$ + HO$_2$. Two separate expressions are given for the rate constant for the HO$_2$ + HO$_2$ reaction. The effective rate constant is given by the sum of these two equations. This reaction has been shown to have a pressure independent bimolecular component and a pressure dependent termolecular component. Both components have negative temperature coefficients. The bimolecular expression is obtained from data of Cox and Burrows (1979), Thrush and Tyndall (1982a,b), Kircher and Sander (1984), Takacs and Howard (1984, 1986), Sander (1984) and Kurylo et al (1986). Data of Rozenshtein et al (1984) are consistent with the low pressure recommendation but they report no change in k with pressure up to 1 atm. Earlier results of Thrush and Wilkinson (1979) are inconsistent with the recommendation. The termolecular expression is obtained from data of Sander et al (1982), Simonaitis and Heicklen (1982) and Kurylo et al (1986) at room temperature and Kircher and Sander (1984) for the temperature dependence. This equation applies to M = air. On this reaction system there is general agreement among investigators on the following aspects of the reaction at high pressure (P ~1 atm): (a) the HO$_2$ uv absorption cross section: Paukert and Johnston (1972), Cox and Burrows (1979), Hochanadel et al (1980), Sander et al (1982), and Kurylo et al (1987a); (b) the rate constant at 300 K: Paukert and Johnston (1972), Hamilton and Lii (1977), Cox and Burrows (1979), Lii et al (1979), Tsuchiya and Nakamura (1979), Sander et al (1982), Simonaitis and Heicklen (1982), and Kurylo et al (1986) (all values fall in the range (2.5 to 4.7) x 10^{-12} cm^3 molecule^1 s^{-1}); (c) the rate constant temperature dependence: Cox and Burrows (1979), Lii et al (1979), and Kircher and Sander (1984); (d) the rate constant water vapor dependence: Hamilton (1975), Hochanadel et al (1972), Hamilton and Lii (1977), Cox and Burrows (1979), DeMore (1979), Lii et al (1981), and Sander et al (1982); (e) the H/D isotope effect: Hamilton and Lii (1977) and Sander et al (1982); and (f) the formation of H$_2$O$_2$ + O$_2$ as the major products at 300 K: Su et al (1979b), Niki et al (1980), Sander et al (1982), and Simonaitis and Heicklen (1982). Sahetchian et al (1982, 1987) give evidence for the formation of a small amount of H$_2$ (~10%) at temperatures near 500 K but Baldwin et al (1984) and Ingold (1988) give evidence that the yield must be much less. Glinski and Birks (1985) report an upper limit of 1% H$_2$ yield at a total pressure of about 50 torr and 298 K but their experiment may have interference from wall reactions. For systems containing water vapor, the factors given by Lii et al (1981) and Kircher and Sander (1984) can be incorporated: $1 + 1.4$ x 10^{-21} [H$_2$O] exp(2200/T). Lightfoot et al (1988) reported atmospheric pressure measurements over the temperature range 298-777 K that are in agreement with the recommended value at room temperature but indicate an upward curvature in the Arrhenius plot at elevated temperatures.

B12. $HO_2 + O_3$. There are four studies of this reaction using flow tube reactors: Zahniser and Howard (1980) at 245 to 365 K, Manzanares et al (1986) at 298 K, and Sinha et al (1987) at 243 to 413 K, and Wang et al (1988) at 233 to 400 K. The data of Sinha et al was given somewhat greater weight in the evaluation because this study did not employ a OH radical scavenger. The other studies fall close to the recommendation. All of the temperature dependence studies show some curvature in the Arrhenius plot with the E/R decreasing at lower temperature. The recommendation incorporates only data at temperatures less than 300 K and is not valid for T > 300 K and is uncertain at T < 230 K, where there are no data. High quality low temperature data are needed for this reaction. Indirect studies using the $HO_2 + HO_2$ reaction as a reference (Simonaitis and Heicklen, 1973; DeMore and Tschuikow-Roux, 1974; and DeMore, 1979) give results that fall below the recommendation, when current data are used for the reference rate coefficient.

C1. $N + O_2$. Changed from JPL 87-41. The recommended expression is derived from a least squares fit to the data of Kistiakowsky and Volpi (1957), Wilson (1967), Becker et al (1969), Westenberg et al (1970), Clark and Wayne (1970), Winkler et al (1986) and Barnett et al (1987). k(298 K) is derived from the Arrhenius expression and is in excellent agreement with the average of all of the room temperature determinations.

C2. $N + O_3$. Changed from JPL 87-41. The recommendation is based on the results of Barnett et al (1987). The value of $(1.0\pm0.2) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} reported by Barnett et al should probably be considered an upper limit rather than a determination. The low values reported by Barnett et al, Stief et al (1979) and Garvin and Broida (1963) cast doubt on the much faster rates reported by Phillips and Schiff (1962), and Chen and Taylor (1961).

C3. $N + NO$. Recommendation is based on the results of Lee et al (1978c). A recent study of Husain and Slater (1980) reports a room temperature rate constant 30 percent higher than the recommended value.

C4. $N + NO_2$. The Panel accepts the results of Clyne and Ono (1982) for the value of the rate constant at 298 K. This is a factor of 2 higher than that reported by Clyne and McDermid (1975). However, Clyne and Ono consider that the more recent study is probably more reliable. Husain and Slater (1980) reported a room temperature rate constant of 3.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, which is a factor of 12 greater than the value reported by Clyne and Ono. This high value may indicate the presence of catalytic cycles, as discussed by Clyne and McDermid, and Clyne and Ono. There are no studies of the temperature dependence of the rate constant. The reaction products are taken to be $N_2O + O$ (Clyne and McDermid). A recent study by Iwata et al (1986) suggested an upper limit of 3.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for the corresponding reaction involving $N(^2D)$ and $N(^2P)$ atoms (sum of all reaction channels).

C5. $O + NO_2$. k(298 K) is based on the results of Davis et al (1973a), Slanger et al (1973), Bemand et al (1974), Ongstad and Birks (1986) and Geers-Muller and Stuhl (1987). The recommendation for E/R is from Davis et al, Ongstad and Birks, and Geers-Muller and Stuhl with the A-factor adjusted to give the recommended k(298 K) value.

C6. $O + NO_3$. Based on the study of Graham and Johnston (1978) at 298 K and 329 K. While limited in temperature range, the data indicate no temperature dependence. Furthermore, by analogy with the reaction of O with NO_2, it is assumed that this rate constant is independent of temperature. Clearly, temperature dependent studies are needed.

C7. $O + N_2O_5$. Based on Kaiser and Japar (1978).

C8. $O + HNO_3$. The upper limit reported by Chapman and Wayne (1974) is accepted.

C9.   O + HO$_2$NO$_2$. The recommended value is based on the study of Chang et al (1981). The large uncertainty in E/R and k at 298 K are due to the fact that this is a single study.

C10. O$_3$ + NO. The recommended Arrhenius expression is a least squares fit to the data reported by Birks et al (1976), Lippmann et al (1980), Ray and Watson (1981b), Michael et al (1981) and Borders and Birks (1982) at and below room temperature, with the data at closely spaced temperatures reported in Lippmann et al and Borders and Birks being grouped together so that these five studies are weighted equally. This expression fits all the data within the temperature range 195-304 K reported in these five studies to within 20 percent. Only the data between 195 and 304 K were used to derive the recommended Arrhenius expression, due to the observed non-linear Arrhenius behavior (Clyne et al (1964), Clough and Thrush (1967), Birks et al, Michael et al and Borders and Birks). Clough and Thrush, Birks et al, Schurath et al (1981), and Michael et al have all reported individual Arrhenius parameters for each of the two primary reaction channels. The range of values for k at stratospheric temperatures is somewhat larger than would be expected for such an easy reaction to study. The measurements of Stedman and Niki (1973a) and Bemand et al (1974) at 298 K are in excellent agreement with the recommended value of k at 298 K.

C11. NO + HO$_2$. The recommendation for HO$_2$ + NO is based on the average of six measurements of the rate constant near room temperature: Howard and Evenson (1977), Leu (1979b), Howard (1979), Glaschick-Schimpf et al (1979), Hack et al (1980), and Thrush and Wilkinson (1981a). All of these are in quite good agreement. An earlier study, Burrows et al (1979), has been dropped because of an error in the reference rate constant, k(OH + H$_2$O$_2$). The room temperature study of Rozenshtein et al (1984) has also been disregarded due to an inadequate discussion of possible secondary reactions. The temperature dependence is from Howard (1980) and is in reasonable agreement with that given by Leu (1979b). A high pressure study is needed in view of the many unusual effects seen in other HO$_2$ reactions.

C12. NO + NO$_3$. The 298 K recommendation is based on the studies of Torabi and Ravishankara (1984), Hammer et al (1986) and Sander and Kircher (1986), which are in excellent agreement. The T dependence is based on an average of the results from Sander and Kircher, and the data of Hammer et al below 300 K.

C13. OH + NO$_3$. New Entry. The recommendation is derived from an average of the results of Boodaghians et al (1988) and the 298 K results of Mellouki et al (1988). The reaction products are probably HO$_2$ + NO$_2$.

C14. OH + HNO$_3$. The intensive study of this reaction over the past few years has significantly reduced many of the apparent discrepancies among (a) the early studies yielding a low, temperature independent rate constant (Smith and Zellner, 1975 and Margitan et al, 1975); (b) more recent work (mostly flash photolysis) with a k(298) approximately 40% larger, and a strong negative T dependence below room temperature (Wine et al, 1981b; Kurylo et al, 1982a; Margitan and Watson, 1982; Marinelli and Johnston, 1982a; Ravishankara et al, 1982; Jourdain et al, 1982; C. A. Smith et al, 1984; Jolly et al, 1985 (298 K), Stachnik et al, 1986); and (c) recent discharge low studies yielding the lower value for k(298 K) but showing substantial negative T dependence (Devolder et al, 1984: Connell and Howard, 1985). Major features of the data are (1) a strong negative T dependence below room temperature, (2) a much weaker temperature dependence above room temperature, possibly leveling off around 500 K, (3) small, measurable pressure dependence which becomes greater at low temperatures. The pressure dependence has been determined by Margitan and Watson (1982) over the ranges 20-100 torr and 225-298 K and by Stachnik et al (1986) at pressures of 10, 60 and 730 torr at 298 K. The two studies are in excellent agreement. Their "low pressure limit" agrees well with the average k(298 K) = 1.0 x 10^{-13} cm^3 s^{-1} derived from the four low pressure discharge flow studies. The values measured for pressures typical of the other flash photolysis studies (20-50 torr) also agree well. The two pressure dependence studies indicate that the high pressure limit

is approximately 50% greater than the low pressure limit at 298 K, and about a factor of 2 greater at 240 K. Thus, over the narrow pressure ranges explored in most flash photolysis studies, the P dependence would escape notice. For temperatures below 300 K, the pressure and temperature dependence can be represented by combining a low pressure (bimolecular) limit, k_o, with a Lindemann-Hinshelwood expression for the P dependence:

$$k(M,T) = k_o + \frac{k_3[M]}{1 + \dfrac{k_3[M]}{k_2}} \quad \text{with} \quad \begin{cases} k_o = 7.2 \times 10^{-15} \exp(785/T) \\ k_2 = 4.1 \times 10^{-16} \exp(1440/T) \\ k_3 = 1.9 \times 10^{-33} \exp(725/T) \end{cases}$$

The coefficients k_3 and k_2 are the termolecular and high pressure limits for the "association" channel. The value of k at high pressures is the sum $k_o + k_2$. The weak pressure dependence and weak T dependence above 300 K explain many of the apparent discrepancies for all the data (including the 1975 studies), except for a few minor features which are probably due to the normally encountered experimental scatter. The Smith and Zellner flash photolysis values are low compared to other flash systems (closer to the flow studies), although the difference is not unusual (~30%). Conversely, the Jourdain et al flow study is high relative to the other ones. The Connell and Howard T dependence (below 300 K) is significantly weaker than the other studies. The failure of Smith et al to observe a pressure effect between 50 and 760 torr, even at 240 K, is in sharp conflict with the effect seen by Stachnik et al over the same range in a much more detailed study. Jolly et al, also could not detect a pressure dependence between 1 torr (M = HNO_3) and 600 torr (M = SF_6) at 298 K. Nelson et al (1981), Jourdain et al and Ravishankara et al have all shown that within experimental error the yield of NO_3 (per OH removed) is unity at 298 K, with similar results at 250 K (Ravishankara et al).

C15. OH + HO_2NO_2. The recommendation for both k at 298 K and the Arrhenius expression is based upon the data of Trevor et al (1982), Barnes et al (1981), C. A. Smith et al (1984) and Barnes et al (1986b). Trevor et al studied this reaction over the temperature range 246-324 K and reported a temperature invariant value of 4.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, although a weighted least squares fit to their data yields an Arrhenius expression with an E/R value of (193±193) K. In contrast, Smith et al studied the reaction over the temperature range 240-300 K and observed a negative temperature dependence with an E/R value of -(650±30) K. The early Barnes et al study (1981) was carried out only at room temperature and 1 torr total pressure while their most recent study was performed in the pressure range 1-300 torr N_2 and temperature range 268-295 K with no rate constant variation being observed. In addition, k_{298} derived in Barnes et al (1981) was revised upward in the later study from 4.1×10^{-12} to 5.0×10^{-12} due to a change in the rate constant for the reference reaction. The values of k at 298 K from the four studies are in excellent agreement. An unweighted least squares fit to the data from the above-mentioned studies yields the recommended Arrhenius expression. The less precise value for k at 298 K reported by Littlejohn and Johnston (1980) is in fair agreement with the recommended value. The error limits on the recommended E/R are sufficient encompass the results of both Trevor et al and Smith et al. It should be noted that the values of k at 220 K deduced from the two studies differ by a factor of 2. Clearly additional studies of k as a function of temperature and the identification of the reaction products are needed.

C16. HO_2 + NO_3. New Entry. The recommendation at 298 K is obtained from a least squares fit to the 298 K data of Mellouki et al (1988) and the temperature dependence data of Hall et al (1988) below 333 K.

C17. O_3 + NO_2. Changed from 87-41. The recommended expression is derived from a least squares fit to the data of Davis et al (1974b), Graham and Johnston (1974), Huie and Herron (1974) and Cox and Coker (1983). The data of Verhees and Adema (1985) and Stedman and Niki (1973a) were not considered because of systematic discrepancies with the other studies.

C18. O_3 + HNO_2. Based on Kaiser and Japar (1977) and Streit et al (1979).

C19. NO_2 + NO_3. New Entry. The existence of the reaction channel forming NO + NO_2 + O_2 has not been firmly established. There are, however, consistent results from three studies (Daniels and Johnston (1921), Johnston and Tao (1951) and Cantrell et al (1988)) which suggest the existence of a bimolecular channel. The results for k_{19} from these studies are given by an expression that is relative to the equilibrium NO_2 + NO_3 + M $\rightleftharpoons$ N_2O_5 + M (see Note 10, Table 2). Using the recommended value for this equilibrium constant, k_{19} is determined to be 8.2 x 10^{-14} exp(-1480/T) cm^3 molecule^{-1} s^{-1}. A matter of concern is that the activation energy is less than the enthalpy of reaction. The 296 K value of Hjorth et al (1989), 5.1 x 10^{-16} cm^3 molecule^{-1} s^{-1}, lies within the uncertainty of the above expression.

C20. N_2O_5 + H_2O. The recommended value at 298 K is based on the studies of Tuazon et al (1983), Atkinson et al (1986) and Hjorth et al (1987). Sverdrup et al (1987) obtained an upper limit that is a factor of four smaller than that obtained in the other studies, but the higher upper limit is recommended because of the difficulty of distinguishing between homogeneous and heterogeneous processes in the experiment.

C21. OH + NH_3. The recommended value at 298 K is the average of the values reported by Stuhl (1973b), Smith and Zellner (1975), Perry et al (1976b), Silver and Kolb (1980), and Stephens (1984). The values reported by Pagsberg et al (1979) and Cox et al (1975) were not considered because these studies involved the analysis of a complex mechanism and the results are well outside the error limits implied by the above five direct studies. The results of Kurylo (1973) and Hack et al (1974) were not considered because of their large discrepancies with the other direct studies (factors of 3.9 and 1.6 at room temperature, respectively). The temperature dependence is based on the results reported by Smith and Zellner, Perry et al, Silver and Kolb, and Stephens, and the pre-exponential factor has been selected to fit the recommended room temperature value.

C22. NH_2 + HO_2. There is a fairly good agreement on the value of k at 298 K between the direct study of Kurasawa and Lesclaux (1980b), and the relative studies of Cheskis and Sarkisov (1979) and Pagsberg et al (1979). The recommended value is the average of the values reported in these three studies. The identity of the products is not known; however, Kurasawa and Lesclaux suggest that the most probable reaction channels give either NH_3 + O_2 or HNO + H_2O as products.

C23. NH_2 + NO. The recommended value for k at 298 K is the average of the values reported by Gordon et al (1971), Gehring et al (1973), Lesclaux et al (1975), Hancock et al (1975), Sarkisov et al (1978), Hack et al (1979b), Stief et al (1982), Silver and Kolb (1982), and Whyte and Phillips (1983). The values reported in these studies for k at 298 K range from 8.3 to 27.0 (x 10^{-12}) cm^3 molecule^{-1} s^{-1}, which is not particularly satisfactory. The results tend to separate into two groups. The flash photolysis results average 1.9 x 10^{-11} cm^3 molecule^{-1} s^{-1}, while those obtained using the discharge flow technique average 0.9 x 10^{-11} cm^3 molecule^{-1} s^{-1}. The apparent discrepancy cannot simply be due to a pressure effect as the pressure ranges of the flash photolysis and discharge flow studies overlapped, and none of the studies observed a pressure dependence for k. There have been four studies of the temperature dependence of k. Each study reported k to decrease with increasing temperature, i.e. $T^{-1.25}$ (Lesclaux et al from 300-500 K), $T^{-1.85}$ (Hack et al from 210-503 K), $T^{-1.67}$ (Stief et al from 216-480 K) and $T^{-2.3}$ exp(-684/T) (Silver and Kolb from 294-1215 K). The recommended temperature dependence is taken to be a weighted average of the data below 500 K from all four studies. The expression is: k = 1.6 x 10^{-11} (T/298)$^{-1.5}$ for the temperature range 210-500 K.

There are many possible product channels for this reaction. Strong evidence against the formation of H atoms exists. Both Silver and Kolb (1982) and Andresen et al (1982) report substantial yields of OH of 40% and ≥65%, respectively, in disagreement with Stief et al (1982), Hall et al (1986) and Dolson (1986) who observed room temperature OH yields of <22%, 13±2% and <15%, respectively. In addition, Andresen et al set a lower limit of ≥29% for the channel $N_2 + H_2O$.

C24. $NH_2 + NO_2$. There have been four studies of this reaction (Hack et al (1979b), Kurasawa and Lesclaux (1979), Whyte and Phillips (1983) and Xiang et al, 1985). There is very poor agreement among these studies both for k at 298 K (factor of 2.3) and for the temperature dependence of k ($T^{-3.0}$ and $T^{-1.3}$). The recommended values of k at 298 K and the temperature dependence of k are averages of the results reported in these four studies. Hack et al have shown that the predominant reaction channel (>95%) produces $N_2O + H_2O$. Just as for the $NH_2 + NO$ reaction, the data for this reaction seem to indicate a factor of two discrepancy between flow and flash techniques, although the data base is much smaller.

C25. $NH_2 + O_2$. The recommendation is based on the reported upper limits of 3×10^{-18} (Lesclaux and Demissy, 1977), 8×10^{-15} (Pagsberg et al, 1979), 1.5×10^{-17} (Cheskis and Sarkisov, 1979), 3×10^{-18} (Lozovsky et al, 1984), 1×10^{-17} (Patrick and Golden, 1984b) and 7.7×10^{-18} (Michael et al, 1985b) all expressed as bimolecular rate constants with units of $cm^3 s^{-1}$. The termolecular rate constant upper limit would be $2 \times 10^{-36} cm^6 s^{-1}$. The values reported by Hack et al (1982), k = 3.6×10^{-33} $(T/295)^{-2} cm^6 s^{-1}$ and Jayanty et al (1976), k = $4 \times 10^{-15} cm^3 s^{-1}$ are not used in arriving at the recommendation. Hack and Kurzke (1985) have observed a reaction between NH_2 and $O_2(^1\Delta)$, obtaining a rate constant of $(1 \pm 0.3) \times 10^{-14} cm^3 molecule^{-1} s^{-1}$ between 295 and 353 K.

C26. $NH_2 + O_3$. Changed from JPL 87-41. There is poor agreement among the recent study of Chekis et al (1985), k(298) = $1.5 \times 10^{-13} cm^3 s^{-1}$, and the earlier studies by Patrick and Golden (1984b), k(298) = $3.25 \times 10^{-13} cm^3 s^{-1}$, Hack et al (1981), $1.84 \times 10^{-13} cm^3 s^{-1}$; Bulatov et al (1980), $1.2 \times 10^{-13} cm^3 s^{-1}$, and Kurasawa and Lesclaux (1980a), $0.63 \times 10^{-13} cm^3 s^{-1}$. The very low value of Kurasawa and Lesclaux may be due to regeneration of NH_2 from secondary reactions (see Patrick and Golden), and it is disregarded here. The discharge flow value of Hack et al is nearly a factor of two less than the recent Patrick and Golden flash photolysis value. The large discrepancy between Bulatov et al and Patrick and Golden eludes explanation. The recommendation is the k(298) average of these four studies, and E/R is an average of Patrick and Golden (1151 K) with Hack et al (710 K).

D1. OH + CO. The recommendation allows for an increase in k with pressure. The zero pressure value was derived by averaging all direct low pressure determinations (those listed in Baulch et al (1980) and the values reported by Dreier and Wolfrum, 1980; Husain et al, 1981; Ravishankara and Thompson, 1983; Paraskevopoulos and Irwin, 1984; Hofzumahaus and Stuhl, 1984; Fritz and Zellner, private communication, 1987). The results of Jonah et al (1984) are too high and were not included. An increase in k with pressure has been observed by a large number of investigators (Overend and Paraskevopoulos, 1977a; Perry et al, 1977; Chan et al, 1977; Bierman et al, 1978; Cox et al, 1976b; Butler et al, 1978; Paraskevopoulos and Irwin, 1982b, 1984; DeMore, 1984; Hofzumahaus and Stuhl, 1984; Fritz and Zellner, 1987; Hynes et al, 1986a; Stachnik and Molina, private communication, 1987; and Wahner and Zetzsch, private communication, 1987). In addition, Niki et al (1984) have measured k relative to OH + C_2H_4 in one atmosphere of air by following CO_2 production using FTIR. The recommended 298 K value was obtained by using a weighted non-linear least squares analysis of all pressure dependent data in N_2 (Paraskevopoulos and Irwin, 1984; DeMore, 1984; Hofzumahaus and Stuhl, 1984; and Hynes et al, 1986a) as well as those in air (Fritz and Zellner, 1987; Niki et al, 1984; Hynes et al, 1986a; Stachnik and Molina, 1987; Wahner and Zetzsch, 1987) to the form k = (A+BP)/(C+DP) where P is pressure in atmospheres. The data were best fit with D = 0 and therefore a linear form is recommended. Previous controversy regarding the effect of small amounts of O_2 (Bierman et al) has

been resolved and is attributed to secondary reactions (DeMore, 1984; Hofzumahaus and Stuhl, 1984). The results of Butler et al (1978) have to be re-evaluated in the light of refinements in the rate coefficient for the OH + H_2O_2 reaction. The corrected rate coefficient is in approximate agreement with the recommended value. Currently, there are no indications to suggest that the presence of O_2 has any effect on the rate coefficient other than as a third body. The E/R value in the pressure range 50-760 torr has been shown to be essentially zero between 220 and 298 K by Hynes et al (1986a), and Stachnik and Molina (private communications, 1987). Further substantiation of the temperature independence of k at 1 atm. may be worthwhile. The uncertainty factor is for 1 atm. of air. In the presence of O_2, the HOCO intermediate is converted to HO_2 + CO_2 (DeMore, 1984). Beno et al (1985) observe an enhancement of k with water vapor which is in conflict with the flash photolysis studies, e.g., Ravishankara and Thompson (1983), Paraskevopoulos and Irwin (1984), DeMore (1984), and Hynes et al (1986a).

D2. OH + CH_4. This is a well characterized reaction. All temperature dependence studies are in good agreement (Greiner, 1970b; Davis et al, 1974a; Margitan et al, 1974; Zellner and Steinert, 1976; Tully and Ravishankara, 1980; Jeong and Kaufman, 1982; Jonah et al, 1984; and Madronich and Felder, 1985). Due to this good agreement, and the curved nature of the Arrhenius plot at higher temperatures, the value of Davis et al obtained in the temperature interval 240 <T <373 K is recommended. It is worth noting that the rate coefficient is small and hence the measurements are easily influenced by impurities. Further, there are only a few measurements below room temperature. Hence, the low temperature values could be slightly lower than those recommended here.

D3. OH + $^{13}CH_4$ (k_{13}). This reaction has been studied relative to the OH + CH_4 (k_{12}) reaction, since the ratio of the rate coefficients k_{13}/k_{12} is the quantity needed for identifying methane sources. Rust and Stevens (1980) obtained a value of 1.003 for $k_{13/12}$ at 298 K while the recent measurement of Davidson et al (1987) yields 1.010±0.007 at the same temperature. No data on the temperature dependence of k_{13}/k_{12} is available. We have recommended the value measured by Davidson et al since they present some reasons as to why Rust and Stevens' value could be low. The error bar is 1.010±0.007 and it overlaps with the measured value of Rust and Stevens.

D4. OH + C_2H_6. There is good agreement among nine studies of this reaction at 298 K, i.e., Greiner (1970a), Howard and Evenson (1976b), Overend et al (1975), Lee and Tang (1982), Leu (1979b), Tully et al (1983), Jeong et al (1984), Tully et al (1986), and Nielsen et al (1986). All these studies were not carried out at exactly 298 K. Therefore, we have recalculated the 298 K value, by assuming an E/R of 1100 K, for those studies where the room temperature was not 298 K. The average of these nine measurements is k(298 K). The temperature dependence was computed by using the data of Greiner (1970a), Tully et al (1983), and Jeong et al (1984). Higher temperature results of Baulch et al (1983), and Tully et al (1986) are in agreement with the recommended value. Recent measurements by Wallington et al (1987b) over the temperature range 234-438 K are in good agreement with the recommended values. Frequently this rate coefficient is measured to check the reliability of new apparatus, and those reported values are not always included in evaluating this k.

D5. OH + C_3H_8. There are many measurements of the rate coefficient at 298 K. In this evaluation we have considered only the direct measurements that are reported in the literature. These are measurements by Greiner (1970a), Tully et al (1983), Droege and Tully (1986), Schmidt et al (1985), Baulch et al (1985), and Bradley et al (1973). The 298 K value is the average of these six studies. Greiner (1970a), Tully et al (1983), and Droege and Tully (1986) have measured the temperature dependence of this reaction, and the recommended E/R was obtained from a linear least squares analysis of the data from these studies at T below 500 K. The A-factor was adjusted to reproduce k(298 K). This reaction has two possible channels, i.e., abstraction of the primary or the secondary H-atom. Therefore, non-Arrhenius behavior is exhibited over a wide temperature range,

as shown by Tully et al., and Droege and Tully. The branching ratios were estimated from the latter:

$$k_{primary} = 6.3 \times 10^{-12} \exp(-1050/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{secondary} = 6.3 \times 10^{-12} \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These numbers are in reasonable agreement with the older data of Greiner.

D6. OH + H_2CO. The value for k(298 K) is the average of those determined by Atkinson and Pitts (1978), Stief et al (1980), Temps and Wagner (1984) and Zabarnick et al (1988). The value reported by Morris and Niki (1971) agrees within the stated uncertainty. There are two relative values which are not in agreement with the recommendations. The value of Niki et al (1978b) relative to OH + C_2H_4 is higher while the value of Smith (1978) relative to OH + OH is lower. The latter data are also at variance with the negligible temperature dependence observed in the two flash photolysis studies. The combined data set suggests E/R = 0. The abstraction reaction shown in the table is the major channel (Temps and Wagner, 1984; Niki et al, 1984); other channels may contribute to a small extent (Horowitz et al, 1978).

D7. OH + CH_3OH. New Entry. The recommended value for k(298 K) is the average of seven direct studies by Overend and Paraskevopoulos (1978), Ravishankara and Davis (1978), Hagele et al (1983), Meier et al (1984), Greenhill and O'Grady (1986), Wallington and Kurylo (1987), and Hess and Tully (1989). Indirect measurements by Campbell et al (1976), Barnes et al (1982), Tuazon et al (1983) and Klopffer et al (1986) are in good agreement with the recommended value. The temperature dependence of k has been measured by Hagele et al, Meier et al, Greenhill and O'Grady, Wallington and Kurylo, and Hess and Tully. The recommended value of E/R was calculated using the results obtained in the temperature range of 240 to 400 K by Greenhill and O'Grady (1986) and Wallington and Kurylo (1987), the only investigators who have measured k below 298 K. Hess and Tully report a curved Arrhenius plot over the temperature range 298 - 1000 K, while Meier et al do not observe such a curvature. This reaction has two pathways; abstraction of the H-atom from the methyl group or from the OH group. The results of Hagele et al, Meier et al, and Hess and Tully suggest that H abstraction from the methyl group is the dominant channel below room temperature.

D8. OH + C_2H_5OH. New Entry. The recommended value for k(298 K) is the average of those reported by Campbell et al (1976), Overend and Paraskevopoulos (1978), Ravishankara and Davis (1978), Cox and Coldstone (1982), Kerr and Stocker (1986), Wallington and Kurylo (1987), Hess and Tully (1988), and Lorenz et al (private communication). The value reported by Meier et al, is nearly a factor of two lower than that recommended here. The recommended value of E/R was obtained by using the data of Lorenz et al, Wallington and Kurylo, and Hess and Tully. At atmospheric temperatures, H-atom abstraction from the CH_2 group is the dominant channel (Meier et al, 1985; Hess and Tully, 1988).

D9. OH + CH_3CHO. There are six measurements of this rate coefficient at 298 K, Morris et al (1971), Niki et al (1978b), Atkinson and Pitts (1978), Kerr and Sheppard (1981), Semmes et al (1985), and Michael et al (1985a). The recommended value of k(298 K) is the average of these measurements. Atkinson and Pitts, Semmes et al, and Michael et al measured the temperature dependence of this rate coefficient and found it to exhibit a negative temperature dependence. The recommended value of E/R is the average E/R of these studies. The A-factor has been adjusted to yield the recommended value of k(298 K).

D10. OH + CH_3OOH. The recommended value for k(298 K) is the average of the rate coefficients measured by Niki et al (1983) and Vaghjiani and Ravishankara (1989) which differ by nearly a factor of two. Niki et al measured the rate coefficient relative to that for OH with C_2H_4 (= 8.0×10^{-12} cm^3 molecule^{-1} s^{-1}) by monitoring CH_3OOH disappearance using an FTIR system. Vaghjiani and Ravishankara monitored the disappearance of OH, OD and [18]OH in excess CH_3OOH in a pulsed

photolysis-LIF system. They measured k between 203 and 423 K and report a negative activation energy with E/R = -190 K. The reaction of OH with CH_3OOH occurs via abstraction of H from the oxygen end to produce the CH_3OO radical and from the CH_3 group to produce the CH_2OOH radical, as originally proposed by Niki et al and confirmed by Vaghjiani and Ravishankara. CH_2OOH is unstable and falls apart to CH_2O and OH within a few microseconds. Its possible reaction with O_2 is unimportant under atmospheric conditions (Vaghjiani and Ravishankara). The recommended branching ratios are,

$$OH + CH_3OOH \rightarrow CH_3O_2 + H_2O \quad (a) \quad 70\%$$

and

$$OH + CH_3OOH \rightarrow CH_2OOH + H_2O \quad (b) \quad 30\%,$$
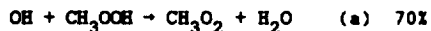
(from Vaghjiani and Ravishankara) and are nearly independent of temperature.

D11. OH + HCN. This reaction is pressure dependent. The recommended value is the high pressure limit measured by Fritz et al (1984) using a laser photolysis-resonance fluorescence apparatus. Phillips (1978) studied this reaction using a discharge flow apparatus at low pressures and found the rate coefficient to have reached the high pressure limit at ~10 torr at 298 K. Fritz et al's results contradict this finding. They agree with Phillip's measured value, within a factor of two, at 7 torr but they find k to increase further with pressure. The products of the reaction are unknown. The measured A-factor appears to be low.

D12. OH + CH_3CN. This rate coefficient has been measured as a function of temperature by Harris et al (1981) between 298 and 424 K, Kurylo and Knable (1984) between 250 and 363 K, and Rhasa and Zellner (private communication, 1987) between 295 and 520 K. In addition, the 298 K value has been measured by Zetzsch (private communication, 1987) and Poulet et al (1984a). The 298 K results of Harris et al are in disagreement with all other measurements and therefore have not been included. The recommended 298 K value is the average of all other studies. The temperature dependence was computed using the results of Kurylo and Knable (250-363 K) and the lower temperature values (i.e., 295-391 K) of Rhasa and Zellner. Two points are worth noting: (a) Rhasa and Zellner observe a curved Arrhenius plot even in the temperature range of 295-520 K and therefore extrapolation of the recommended expression could lead to large errors, and (b) Zetzsch observed a pressure dependent increase at k(298 K) which levels off at about 1 atmosphere. This observation is contradictory to the results of other investigations. A complex reaction mechanism cannot be ruled out. The products of the reaction are unknown.

D13. O_3 + C_2H_2. New Entry. The data base for this reaction is not well established. Room temperature measurements (Cadle and Schadt, 1953; DeMore, 1969; DeMore, 1971; Stedman and Niki, 1973b; Pate et al, 1976; and Atkinson and Aschmann, 1984) disagree by as much as an order of magnitude. It is probable that secondary reactions involving destruction of ozone by radical products resulted in erroneously high values for the rate constants in several of the previous measurements. The present recommendation for k(298K) is based on the room temperature value of Atkinson and Aschmann (1984), which is the lowest value obtained and therefore perhaps the most accurate. The temperature dependence is estimated, based on an assumed A-factor of 1.0×10^{-14} cm^3 s^{-1} similar to that for the O_3 + C_2H_4 reaction and corresponding to the expected 5-membered ring structure for the transition state (DeMore, 1969, 1971). Further studies, particularly of the temperature dependence, are needed. Major products in the gas phase reaction are CO, CO_2, and HCOOH, and chemically-activated formic anhydride has been proposed as an intermediate of the reaction (DeMore, 1971, and DeMore and Lin, 1973). The anhydride intermediates in several alkyne ozonations have been isolated in low temperature solvent experiments (DeMore and Lin, 1971).
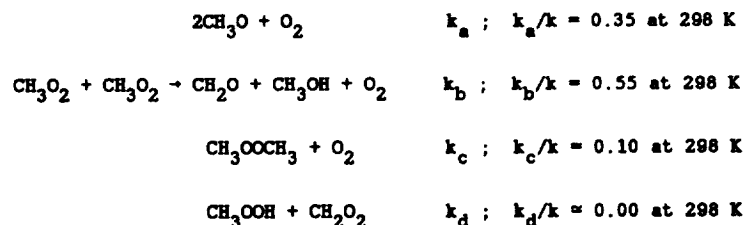
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D14. O_3 + C_2H_4. New Entry. The rate constant of this reaction is well established over a wide temperature range, 178 to 360 K. Our recommendation is taken from that of IUPAC (1989), which is based on the data of DeMore (1969), Stedman et al (1973), Herron and Huie (1974), Japar et al (1974, 1976), Toby et al (1976), Su et al (1980), Adeniji et al (1981), Kan et al (1981), Atkinson et al (1982), and Bahta et al (1984).

D15. O_3 + C_3H_6. New Entry. The rate constant of this reaction is well established over the temperature range 185 to 360 K. The present recommendation is based largely on the data of Herron and Huie (1974), in the temperature range 235-362 K. (Note that a typographical error in Table 2 of that paper improperly lists the lowest temperature as 250 K, rather than the correct value, 235 K). The recommended Arrhenius expression agrees within 25% with the low temperature (185-195 K) data of DeMore (1969), and is consistent with, but slightly lower (about 40%) than the data of Adeniji et al (1981) in the temperature range 260-294 K. Room temperature measurements of Cox and Penkett (1972), Stedman et al (1973), Japar et al (1974, 1976), and Atkinson et al (1982) are in good agreement (10% or better) with the recommendation.

D16. HO_2 + CH_2O. There is sufficient evidence to suggest that HO_2 adds to CH_2O (Su et al, 1979b,c; Veyret et al, 1982; Zabel et al, 1987; Barnes et al, 1985; and Veyret et al, 1989). The recommended k298 is the average of values obtained by Su et al (1979c), Veyret et al (1982), and Veyret et al (1989). The temperature dependence observed by Veyret et al (1989) is recommended. The value reported by Barnes et al at 273 K is consistent with this recommendation. The adduct $HO_2 \cdot CH_2O$ seems to isomerize to $HOCH_2OO$ reasonably rapidly and reversibly. There is a great deal of discrepancy between measured values of the equilibrium constants for this reaction.

D17. O + HCN. This reaction has been studied at high temperatures, i.e., T >1000 K, because of its importance in combustion systems, Roth et al (1980), Szekely et al (1984), and Louge and Hanson (1984). Davies and Thrush (1968) studied this reaction between 469 and 574 K while Perry and Melius (1984) studied it between 540 and 900 K. Results of Perry and Melius are in agreement with those of Davies and Thrush. Our recommendation is based on these two studies. This reaction has two reaction pathways: O + HCN → H + NCO, ΔH = -2 kcal/mol (ka); and O + HCN → CO + NH (kb), ΔH = -36 kcal/mol. The branching ration k_a/k_b for these two channels has been measured to be ~2 at T ≃ 860 K. The branching ratio at lower temperatures is unknown.

D18. O + C_2H_2. The value at 298 K is an average of ten measurements; Arrington et al (1965), Sullivan and Warneck (1965), Brown and Thrush (1967), Hoyermann et al (1967, 1969), Westenberg and deHaas (1969b), James and Glass (1970), Stuhl and Niki (1971), Westenberg and deHaas (1977), and Aleksandrov et al (1981). There is reasonably good agreement among these studies. Arrington et al (1965) did not observe a temperature dependence, an observation which was later shown to be erroneous by Westenberg and deHaas (1969b). Westenberg and deHaas (1969b), Hoyermann et al (1969), and Aleksandrov et al (1981) are the only authors who have measured the temperature dependence below 500 K. Westenberg and deHaas observed a curved Arrhenius plot at higher temperature. In the range 195-450 K, Arrhenius behavior provides an adequate description and the E/R obtained by a fit of the data from these three groups in this temperature range is recommended. The A-factor was calculated to reproduce k(298 K). This reaction can have two sets of products, i.e., C_2HO + H or CH_2 + CO. Under molecular beam conditions C_2HO has been shown to be the major product. The study by Aleksandrov et al using a discharge flow-resonance fluorescence method (under undefined pressure conditions) indicates that the C_2HO + H channel contributes no more than 7% to the net reaction at 298 K, while a similar study by Vinickier et al (1985) suggests that both CH_2 and CH_2O are formed.

D19. O + H_2CO. The recommended values for A, E/R and k(298 K) are the averages of those determined by Klemm (1979) using flash photolysis-resonance fluorescence (250 to 498 K), by Klemm et al (1980) using discharge flow-resonance fluorescence (298 to 748 K) and Chang and Barker (1979) using discharge flow-mass spectrometry (296 to 436 K). All three studies are in good agreement. The

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k(298 K) value is also consistent with the results of Niki et al (1969), Herron and Penzhorn (1969), and Mack and Thrush (1973). Although the mechanism for O + H₂CO has been considered to be the abstraction reaction yielding OH + HCO, Chang and Barker suggest that an addition channel yielding H + HCO₂ may be occurring to the extent of 30% of the total reaction. This conclusion is based on an observation of CO₂ as a product of the reaction under conditions where reactions such as O + HCO → H + CO₂ and O + HCO → OH + CO apparently do not occur. This interesting suggestion needs independent confirmation.

D20.   O + CH₃CHO. The recommended k(298 K) is the average of three measurements by Cadle and Powers (1967), Mack and Thrush (1974), and Singleton et al (1977), which are in good agreement. Cadle and Powers and Singleton et al studied this reaction as a function of temperature between 298 K and 475 K and obtained very similar Arrhenius parameters. The recommended E/R value was obtained by considering both sets of data. This reaction is known to proceed via H-atom abstraction (Mack and Thrush, 1974; Avery and Cvetanovic, 1965; and Singleton et al, 1977).

D21.   O + CH₃. The recommended k(298 K) is the weighted average of three measurements by Washida and Bayes (1976), Washida (1980), and Plumb and Ryan (1982b). The E/R value is based on the results of Washida and Bayes (1976), who found k to be independent of temperature between 259 and 341 K.

D22.   CH₃ + O₂. This bimolecular reaction is not expected to be important, based on the results of Baldwin and Golden (1978a), who found k < 5 x 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹ for temperatures up to 1200 K. Klais et al (1979) failed to detect OH (via CH₃ + O₂ → CH₂O + OH) at 368 K and placed an upper limit of 3 x 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ for this rate coefficient. Bhaskaran et al (1979) measured k = 1 x 10⁻¹¹ exp(-12,900/T) cm³ molecule⁻¹ s⁻¹ for 1800 <T <2200 K. The latter two studies thus support the results of Baldwin and Golden. Studies by Selzer and Bayes (1983) and Plumb and Ryan (1982b) confirm the low value for this rate coefficient. Previous studies of Washida and Bayes (1976) are superseded by those of Selzer and Bayes. Plumb and Ryan have placed an upper limit of 3 x 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ based on their inability to find HCHO in their experiments. A recent study by Zellner and Ewig (1988) suggests that this reaction is important at combustion temperatures but is unimportant for the atmosphere.

D23.   C₂H₅ + O₂. New Entry. This recommendation is taken from IUPAC (1989).

D24.   CH₂OH + O₂. The rate coefficient was first measured directly by Radford (1980) by detecting the HO₂ product in a laser magnetic resonance spectrometer. The wall loss of CH₂OH could have introduced a large error in this measurement. Radford also showed that the previous measurement of Avramenko and Kolesnikova (1961) was in error. Wang et al (1984) measured a value of 1.4 x 10⁻¹² cm³ molecule⁻¹ s⁻¹ by detecting the HO₂ product. Recently, Dobe et al (1985), Grotheer et al (1985), Payne et al (1988), Grotheer et al (1988) and Nesbitt et al (1988) have measured k(298 K) to be close to 1.0 x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ under conditions where wall losses are small. The recommended value is the average of these five studies. The result of Wang et al (1984) has been rejected in the face of the new evidence. This reaction appears to exhibit a very complex temperature dependence. Based on the recent data of Grotheer et al (1988) and Nesbitt et al (1988), k appears to increase from 200 K to approximately 250 K in an Arrhenius fashion, levels off at approximately 300 K, decreases from 300 to 500 K, and finally increases as temperature is increased. This complex temperature dependence is believed to be due to the formation of a CH₂(OH)·O₂ adduct which can isomerize to CH₂O·HO₂ or decompose to reactants. The CH₂O·HO₂ isomer can decompose to CH₂O and HO₂ or reform the original adduct. At temperatures less than 250 K, the data of Nesbitt et al suggests an E/R value of ~ 1700 K.

D25.   CH₃O + O₂. The recommended value for k(298 K) is the average of those reported by Lorenz et al (1985) and Wantuck et al (1987). The recommended A-factor and E/R are those obtained using the results of Gutman et al (1982), Lorenz et al (1985), and Wantuck et al (1987) in the

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temperature range 298 to 500 K. These investigators have measured k directly under pseudo-first order conditions by following CH_3O via laser induced fluorescence. The temperature intervals were 413 to 608 K (by Gutman et al), 298 to 450 K (by Lorenz et al), and 298 to 973 K (by Wantuck et al). Cox et al (1980) used an end product analysis technique to measure k down to 298 K. The previous high temperature measurements (Barker et al (1977) and Batt and Robinson (1979)), are in reasonable agreement with the derived expression. k(298 K) is calculated from the recommended expression. This value is consistent with the 298 K results of Cox et al (1980) and with the upper limit measured by Sanders et al (1980b). The A-factor appears to be too low for a hydrogen atom transfer reaction. The Arrhenius plot is curved at higher temperature (Wantuck et al). The reaction may be more complicated than a simple abstraction. The products of this reaction are HO_2 and CH_2O, as shown by Niki et al (1981), which is consistent with a reported CH_2O yield of 0.85±0.15 (Zellner, private communication, 1987).

D26. $HCO + O_2$. The value of k(298 K) is the average of the determinations by Washida et al (1974), Shibuya et al (1977), Veyret and Lesclaux (1981), and Langford and Moore (1984). There are three measurements of k where HCO was monitored via the intracavity dye laser absorption technique (Reilly et al (1978), Nadtochenko et al (1979), and Gill et al (1981)). Even though there is excellent agreement between these three studies, they yield consistently lower values than those obtained by other techniques. There are several possible reasons for this discrepancy: (a) The relationship between HCO concentration and laser attenuation might not be linear, (b) there could have been depletion of O_2 in the static systems that were used (as suggested by Veyret and Lesclaux), and (c) these experiments were designed more for the study of photochemistry than kinetics. Therefore, these values are not included in obtaining the recommended value. The recommended temperature dependence is essentially identical to that measured by Veyret and Lesclaux. We have expressed the temperature dependence in an Arrhenius form even though the authors preferred a T^n form ($k = 5.5 \times 10^{-11} T^{-(0.4\pm0.3)}$ cm^3 molecule^{-1} s^{-1}).

D27. $CH_3 + O_3$. The recommended A-factor and E/R are those obtained from the results of Ogryzlo et al (1981). The results of Simonaitis and Heicklen (1975), based on an analysis of a complex system, are not used. Washida et al (1980b) used $O + C_2H_4$ as the source of CH_3. Recent results (Buss et al (1981), Kleinermanns and Luntz (1981), Hunziker et al (1981), and Inoue and Akimoto (1981)) have shown the $O + C_2H_4$ reaction to be a poor source of CH_3. Therefore, the results of Washida et al are also not used.

D28. $CH_3O_2 + O_3$. There are no direct studies of this reaction. The quoted upper limit is based on indirect evidence obtained by Simonaitis and Heicklen (1975).

D29. $CH_3O_2 + CH_3O_2$. This reaction has been studied at 298 K by Hochanadel et al (1977), Parkes (1977), Anastasi et al (1978), Kan et al (1979), Sanhueza et al (1979), Cox and Tyndall (1980), Sander and Watson (1981c), Jenkin et al (1988), McAdam et al (1987), Kurylo and Wallington (1987), Lightfoot et al (1989a), and Basco and Parmar (1985). All the above determinations used ultraviolet absorption techniques to monitor CH_3O_2 and hence measured k/σ, where σ is the absorption cross section for CH_3O_2 at the monitored wavelength. Therefore, the derived value of k critically depends on the value of σ used. Currently, even though there is good agreement between the measured values of k/σ, there are large discrepancies (approximately a factor of 2) between the values of σ measured by Hochanadel et al, Parkes, Sander and Watson, Adachi et al (1980), McAdam et al (1987), and Kurylo et al (1987a). To obtain the recommended k value at 298 K, an average value of σ at 250 nm, 3.7×10^{-18} cm^2, was chosen. Using this value of σ and the weighted average value of k/σ at 250 nm measured by Cox and Tyndall, Jenkin et al (1988), Sander and Watson, Mc Adams et al, Kurylo and Wallington, and Lightfoot et al (1989), the value of k(298 K) was derived. The recommended temperature dependence is that measured by Sander and Watson (1981c), Kurylo and Wallington (1987), and Lightfoot et al at temperatures between 228 and 420 K, using a value of σ independent of T. It is not clear whether the above procedure of recalculating k using an average value of σ is valid.

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Therefore, the error limits have been increased to encompass the values of k calculated by various authors. This reaction has four possible sets of products, i.e.,

$$2CH_3O + O_2 \qquad k_a \; ; \quad k_a/k = 0.35 \text{ at } 298 \text{ K}$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_2O + CH_3OH + O_2 \qquad k_b \; ; \quad k_b/k = 0.55 \text{ at } 298 \text{ K}$$

$$CH_3OOCH_3 + O_2 \qquad k_c \; ; \quad k_c/k = 0.10 \text{ at } 298 \text{ K}$$

$$CH_3OOH + CH_2O_2 \qquad k_d \; ; \quad k_d/k \simeq 0.00 \text{ at } 298 \text{ K}$$

FTIR studies by Kan et al (1980) and Niki et al (1981) are in reasonable agreement on branching ratios at 298 K; $k_a/k \sim 0.35$, $k_b/k \sim 0.55$. The recent study of Lightfoot et al also yields $k_a/k \simeq 0.35$ at 298 K. These authors see a large decrease of k_a/k with decreasing temperature. Channel (d) was suggested by Nangia and Benson (1980), but there is no experimental data to suggest its occurence. Because of the existence of multiple pathways, the temperature dependence of k may be complex. Further work is required on both the temperature dependence and the variation of branching ratios with temperature. It should be noted that the knowledge of the branching ratio is needed to correct the measured value of k and the above branching ratios have been used in obtaining the recommended value.

D30. CH_3O_2 + NO. The value of k(298 K) is the average of those determined by Sander and Watson (1980), Ravishankara et al (1981a), Cox and Tyndall (1980), Plumb et al (1981), Simonaitis and Heicklen (1981) and Zellner et al (1986). Values lower by more than a factor of two have been reported by Adachi and Basco (1979) and Simonaitis and Heicklen (1979). The former direct study was probably in error because of interference by CH_3ONO formation. The results of Simonaitis and Heicklen (1979) and Plumb et al (1979) are assumed to be superseded by their more recent values. Ravishankara et al (1981a) and Simonaitis and Heicklen (1981) have measured the temperature dependence of k over limited temperature ranges. The recommended A-factor and E/R were obtained by a least squares analysis of the data from the two studies. The value of k(218 K) obtained by Simonaitis and Heicklen (1981) is not included; however, the large error bounds allow the calculated value of k at 218 K to overlap that measured by Simonaitis and Heicklen. Ravishankara et al (1981a) find that the reaction channel leading to NO_2 accounts for at least 80% of the reaction. Zellner et al (1986) have measured the yield of CH_3O to be 1.0±0.2. These results, in conjunction with the indirect evidence obtained by Pate et al (1974), confirm that NO_2 formation is the major, if not the only, reaction path.

D31. CH_3O_2 + HO_2. The rate coefficient at 298 K has been measured by Cox and Tyndall (1979, 1980), Moortgat et al (1986), McAdam et al (1987), Kurylo et al (1987b), Jenkin et al (1988), and Lightfoot et al (1989b). In all the studies, except that of Jenkin et al, both CH_3O_2 and HO_2 have been monitored via UV absorption. Jenkin et al used IR absorption of HO_2 and UV absorption of CH_3O_2 to obtain the rate constant. Because of overlapping absorption spectra of CH_3O_2 and HO_2 and the unavoidable occurrence of the CH_3O_2 + CH_3O_2 and HO_2 + HO_2 reactions along with the CH_3O_2 + HO_2 reaction, the extraction of the rate coefficient requires modelling of the system and reliance on the the UV cross sections of both CH_3O_2 and HO_2. The agreement between the values of k obtained by all these groups is not very good. Part of the differences are definitely due to different values of the UV cross sections used in various studies. Contributions from secondary reactions may also be partly responsible for the differences. Unfortunately, it is not feasible to correct the reported values to a common set of cross sections. Therefore, the average of values from Cox and Tyndall, Moortgat et al, Kurylo and Wallington, Jenkin et al, and Lightfoot et al are used to obtain the recommended value. The results of McAdam et al are believed to be in error due to an instrumental problem (Lightfoot et al, 1989b) and are hence not included. Cox and Tyndall, Dagaut et al (1988a),

and Lightfoot et al. have measured the temperature dependence of this rate coefficient. The recommended E/R was obtained by plotting $\ln (k_{(T)}/k_{298})$ vs 1/T from these studies. This method looks for only the E/R value in each data set. The A factor was calculated to reproduce k_{298}. The studies by the above groups have indicated that this reaction is not affected by pressure or nature of the buffer gas.

The products of this reaction were believed to be only $CH_3OOH + O_2$. However, the recent work of Jenkin et al suggests a substantial fraction of the reaction may yield $H_2O + CH_2O + O_2$. The lower value of k measured by monitoring CH_3OOH formation by Moortgat et al and Kan et al (1980) is consistent with the occurrence of the second channel and the lower value of k measured when CH_3OOH product yield is monitored. Further work on measurement of k without reliance on UV absorption cross sections and branching ratios are needed.

D32. $C_2H_5O_2 + C_2H_5O_2$. New Entry. The recommended value of k(298 K) was derived from the studies of Adachi et al (1979), Anastasi et al (1979), Munk et al (1986), Cattell et al (1986), Anastasi et al (1987), and Wallington et al (1988). All the above determinations used an ultraviolet absorption technique to monitor $C_2H_5O_2$ and hence measured k/σ, where σ is the absorption cross section of $C_2H_5O_2$ at the monitoring wavelength. These investigators also measured the σ that was used in evaluating the rate coefficient. There are large discrepancies between the measured values of σ by the above authors. For this evaluation, we have used the reported value of k rather than evaluating a mean value of k/σ and then converting it to k, using a preferred value of σ. In all these experiments the observed rate coefficient is higher than the true rate coefficient because of secondary reactions involving HO_2. HO_2 is formed by the reaction of C_2H_5O with O_2, and reacts with $C_2H_5O_2$ to enhance the observed rate coefficient (see Wallington et al for further discussion). Based on product branching ratios discussed below, which determine the magnitude of the necessary correction, the recommended rate coefficient is 0.6 times the average observed rate coefficient. The recommended value of E/R was obtained from the results of Adachi et al, Anastasi et al, and Wallington et al. Niki et al (1982) have measured the end products of this reaction in air. The observed products suggest that at 298 K the channel to yield $2 C_2H_5O + O_2$ accounts for more than 50% of the reaction; the channel to yield $CH_3CHO + C_2H_5OH + O_2$ accounts for more than 39% of the reaction; and the channel to yield $C_2H_5O_2C_2H_5 + O_2$ accounts for less than 9% of the reaction. These branching ratios were used above to obtain the true rate coefficient from the observed rate coefficient.

D33. $C_2H_5O_2 + NO$. New Entry. The recommended value is that reported by Plumb et al (1982). The value reported by Adachi and Basco (1979), which is a factor of three lower than the Plumb et al value, was not included. The rate coefficient for the $CH_3O_2 + NO$ reaction measured by Basco's group, using the same apparatus, is much lower than the value recommended here. The temperature dependence of the $C_2H_5O_2 + NO$ rate coefficient has not been measured. However, by analogy with the $CH_3O_2 + NO$ reaction, the expected value of E/R is near zero, with a small negative value being likely.

D34. $C_2H_5O_2 + HO_2$. New Entry. The recommended value is the average of those measured by Cattell et al (1986) and Dagaut et al (1988b). In both experiments the rate coefficient was obtained by modeling the reaction system. Also, the calculated rate coefficients depended on the UV absorption cross sections of both $C_2H_5O_2$ and HO_2. As mentioned earlier, the absorption cross section of $C_2H_5O_2$ is not well-defined. The agreement between the two studies, however, is reasonable. The recommended E/R is that measured by Dagaut et al.

D35. $NO_3 + CO$. The upper limit is based on the results of Ridley and McFarland (private communication, 1984) and Hjorth et al (1986). Ridley and McFarland estimated an upper limit of 1×10^{-20} cm^3 molecule^{-1} s^{-1} based on their measurements of NO_3 loss in excess CO. Hjorth et al obtained an upper limit of 4×10^{-19} cm^3 molecule^{-1} s^{-1} based on an FTIR analysis of isotopically labeled CO loss in the presence of NO_3. Burrows et al (1985b) obtained an upper limit of 4×10^{-16} cm^3 molecule^{-1} s^{-1}, which is consistent with the other two studies. Products are expected to be $NO_2 + CO_2$.

D36. NO_3 + CH_2O. There are three measurements of this rate coefficient at 298 K, Atkinson et al (1984a), Cantrell et al (1985), and Hjorth et al (1988). The value reported by Atkinson et al (1984a), k = (3.23±0.26) x 10^{-16} cm^3 molecule^{-1} s^{-1}, is corrected to 5.8 x 10^{-16} cm^3 molecule^{-1} s^{-1} to account for the different value of the equilibrium constant for the NO_3 + NO_2 ⇌ N_2O_5 reaction that was measured subsequent to this study by the same group using the same apparatus. This correction is in accordance with their suggestion (Tuazon et al, 1984). The value reported by Cantrell et al, and Hjorth et al, k = 6.3 x 10^{-16} cm^3 molecule^{-1} s^{-1} and (5.4±1.1) x 10^{-16} cm^3 molecule^{-1} s^{-1}, respectively, are in good agreement with the corrected value of Atkinson et al. The recommended value is the average of these three studies. Cantrell et al have good evidence to suggest that HNO_3 and CHO are the products of this reaction. The temperature dependence of this rate coefficient is unknown.

D37. NO_3 + CH_3CHO. There are four measurements of this rate constant, Morris and Niki (1974), Atkinson et al (1984a), Cantrell et al (1986), Dlugokencky and Howard (1989). The value reported by Atkinson et al (1984a), k = (1.34±0.28) x 10^{-15} cm^3 molecule^{-1} s^{-1}, is corrected to 2.4 x 10^{-15} cm^3 molecule^{-1} s^{-1} as discussed for the NO_3 + H_2CO reaction above and as suggested by Tuazon et al (1984). The recommended value is the average of the values obtained by Atkinson et al (2.4 x 10^{-15} cm^3 molecule^{-1} s^{-1}), Cantrell et al (2.1 x 10^{-15} cm^3 molecule^{-1} s^{-1}), and Dlugokencky and Howard (2.74 x 10^{-15} cm^3 molecule^{-1} s^{-1}). The results of Morris and Niki agree with the recommended value when their original data is re-analyzed using the currently recommended value for the equilibrium constant for the reaction NO_2 + NO_3 ⇌ N_2O_5 as shown by Dlugokencky and Howard. Dlugokencky and Howard have studied the temperature dependence of this reaction. Their measured value of E/R is recommended. The A-factor has been calculated to yield k(298) recommended here. Morris and Niki, and Cantrell et al observed the formation of HNO_3 and PAN in their studies, which strongly suggests that HNO_3 and CH_3CO are the products of this reaction.

E1. Cl + O_3. The results reported for k(298 K) by Watson et al (1976), Zahniser et al (1976), Kurylo and Braun (1976) and Clyne and Nip (1976a) are in good agreement, and have been used to determine the preferred value at this temperature. The values reported by Leu and DeMore (1976) (due to the wide error limits) and Clyne and Watson (1974a) (the value is inexplicably high) are not considered. The four Arrhenius expressions are in fair agreement within the temperature range 205-300 K. In this temperature range, the rate constants at any particular temperature agree to within 30-40%. Although the values of the activation energy obtained by Watson et al and Kurylo and Braun are in excellent agreement, the value of k in the study of Kurylo and Braun is consistently (~17%) lower than that of Watson et al. This may suggest a systematic underestimate of the rate constant, as the values from the other three agree so well at 298 K. A more disturbing difference is the scatter in the values reported for the activation energy (338-831 cal/mol). However, there is no reason to prefer any one set of data to any other; therefore, the preferred Arrhenius expression shown above was obtained by computing the mean of the four results between 205 and 298 K. Inclusion of higher temperature (≤ 466 K) experimental data would yield the following Arrhenius expression: k = (3.4±1.0) x 10^{-11} exp(-310±76/T). Results of a new study by Nicovich et al (1989) show non-Arrhenius behavior over the temperature range 189-385 K. The new results are in good agreement with the present recommendation above about 250 K, but at lower temperatures they are faster than the recommendation although still within its stated uncertainty down to about 220 K.

Vanderzanden and Birks (1982) have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1-0.5%) of O_2 ($^1\Sigma_g^+$) in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore (1981), in connection with the Cl_2 photosensitized decomposition of ozone. However Choo and Leu (1985) were unable to detect $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ in the Cl + O_3 system and set upper limits to the branching ratios for their production of 5 x 10^{-4} and 2.5 x 10^{-2}, respectively. They suggested two possible mechanisms for the observed production of oxygen atoms, involving reactions of vibrationally excited ClO radicals with O_3 or with Cl atoms, respectively. Burkholder et al (1989) in a study of infrared line

intensities of the ClO radical present evidence in support of the second mechanism. In their experiments with excess Cl atoms, the vibrationally excited ClO radicals produced in the Cl + O_3 reaction can react with Cl atoms to give Cl_2 and oxygen atoms which can then remove additional ClO radicals. These authors point out the possibility for systematic error from assuming a 1:1 stoichiometry for $[ClO]:[O_3]_0$ when using the Cl + O_3 reaction as a quantitative source of ClO radicals for kinetic and spectroscopic studies.

E2. Cl + H_2. This Arrhenius expression is based on the data below 300 K reported by Watson et al (1975), Lee et al (1977), Miller and Gordon (1981), and Kita and Stedman (1982). The results of these studies are in excellent agreement below 300 K; the data at higher temperatures are in somewhat poorer agreement. The results of Watson et al, Miller and Gordon, and Kita and Stedman agree well (after extrapolation) with the results of Benson et al (1969) and Steiner and Rideal (1939) at higher temperatures. For a discussion of the large body of rate data at high temperatures see the review by Baulch et al (1980). Miller and Gordon and Kita and Stedman also measured the rate of the reverse reaction, and found the ratio to be in good agreement with equilibrium constant data.

E3. Cl + CH_4. The values reported from the thirteen absolute rate coefficient studies for k at 298 K fall in the range (0.99 to 1.48) x 10^{-13}, with a mean value of 1.15 x 10^{-13}. However, based upon the stated confidence limits reported in each study, the range of values far exceeds that to be expected. A preferred average value of 1.0 x 10^{-13} can be determined from the absolute rate coefficient studies for k at 298 K by giving equal weight to the values reported in Lin et al (1978a), Watson et al (1976), Manning and Kurylo (1977), Whytock et al (1977), Zahniser et al (1978), Michael and Lee (1977), Keyser (1978), and Ravishankara and Wine (1980). The values derived for k at 298 K from the competitive chlorination studies of Pritchard et al (1954), Knox (1955), Pritchard et al (1955), Knox and Nelson (1959), and Lin et al (1978a) range from (0.95-1.13) x 10^{-13}, with an average value of 1.02 x 10^{-13}. The preferred value of 1.0 x 10^{-13} was obtained by taking a mean value from the most reliable absolute and relative rate coefficient studies.

There have been nine absolute studies of the temperature dependence of k. In general the agreement between most of these studies can be considered to be quite good. However, for a meaningful analysis of the reported studies it is best to discuss them in terms of two distinct temperature regions, (a) below 300 K, and (b) above 300 K. Three resonance fluorescence studies have been performed over the temperature range ~200-500 K (Whytock et al (1977), Zahniser et al (1978) and Keyser (1978)) and in each case a strong nonlinear Arrhenius behavior was observed. Ravishankara and Wine (1980) also noted nonlinear Arrhenius behavior over a more limited temperature range. This behavior tends to explain partially the large variance in the values of E/R reported between those other investigators who predominantly studied this reaction below 300 K (Watson et al (1976) and Manning and Kurylo (1977)) and those who only studied it above 300 K (Clyne and Walker (1973), Poulet et al (1974), and Lin et al (1978a)). The agreement between all studies below 300 K is good, with values of (a) E/R ranging from 1229-1320 K, and (b) k(230 K) ranging from (2.64-3.32) x 10^{-14}. The mean of the two discharge flow values (Zahniser et al (1978) and Keyser (1978)) is 2.67 x 10^{-14}, while the mean of the four flash photolysis values (Watson et al (1976), Manning and Kurylo (1977), Whytock et al (1977), and Ravishankara and Wine (1980)) is 3.22 x 10^{-14} at 230 K. There have not been any absolute studies at stratospheric temperatures other than those which utilized the resonance fluorescence technique. Ravishankara and Wine (1980) have suggested that the results obtained using the discharge flow and competitive chlorination techniques may be in error at the lower temperatures (<240 K) due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic chlorine. Ravishankara and Wine observed that at temperatures below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture; i.e., if the mixture did not contain an efficient spin equilibrator, e.g. Ar or CCl_4, the bimolecular rate constant decreased at high CH_4 concentrations. The chemical composition in each of the flash photolysis studies contained an efficient spin equilibrator, whereas this was not the case in the discharge flow studies. However, the reactor walls in the discharge flow studies could have been expected

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to have acted as an efficient spin equilibrator. Consequently, until the hypothesis of Ravishankara and Wine is proven it is assumed that the discharge flow and competitive chlorination results are reliable.

Above 300 K the three resonance fluorescence studies reported (a) "averaged" values of E/R ranging from 1530-1623 K, and (b) values for k(500 K) ranging from $(7.74-8.76) \times 10^{-13}$. Three mass spectrometric studies have been performed above 300 K with E/R values ranging from 1409-1790 K. The data of Poulet et al (1974) are sparse and scattered, that of Clyne and Walker (1973) show too strong a temperature dependence (compared to all other absolute and competitive studies) and k(298 K) is ~20% higher than the preferred value at 298 K, while that of Lin et al (1978a) is in fair agreement with the resonance fluorescence results.

In conclusion, it should be stated that the best values of k from the absolute studies, both above and below 300 K, are obtained from the resonance fluorescence studies. The competitive chlorination results differ from those obtained from the absolute studies in that linear Arrhenius behavior is observed. This difference is the major discrepancy between the two types of experiments. The values of E/R range from 1503 to 1530 K, and k(230 K) from $(2.11-2.54) \times 10^{-14}$ with a mean value of 2.27×10^{-14}. It can be seen from the above discussion that the average values at 230 K are: 3.19×10^{-14} (flash photolysis), 2.67×10^{-14} (discharge flow) and 2.27×10^{-14} (competitive chlorination). These differences increase at lower temperatures. Until the hypothesis of Ravishankara and Wine (1980) is re-examined, the preferred Arrhenius expression attempts to best fit the results obtained between 200 and 300 K from all sources. The average value of k at 298 K is 1.04×10^{-13}, and at 230 K is 2.71×10^{-14} (this is a simple mean of the three average values). The preferred Arrhenius expression yields values similar to those obtained in the discharge flow-resonance fluorescence studies. If only flash photolysis-resonance fluorescence results are used then an alternate expression of 6.4×10^{-12} (exp(-1200/T)) can be obtained (k(298 K) = 1.07×10^{-13}, and k(230 K) = 3.19×10^{-14}).

A study (Heneghan et al (1981)) using very low pressure reactor techniques reports results from 233 to 338 K in excellent agreement with the other recent measurements. They account for the curvature in the Arrhenius plot at higher temperatures by transition state theory. Measured equilibrium constants are used to derive a value of the heat of formation of the methyl radical at 298 K of 35.1±0.1 kcal/mol. The result of a similar study (Dobis and Benson (1987)) at room temperature is in excellent agreement with the recommended value.

E4.   Cl + C_2H_6. The absolute rate coefficients reported in all four studies (Davis et al (1970), Manning and Kurylo (1977), Lewis et al (1980), and Ray et al (1980)) are in good agreement at 298 K. The value reported by Davis et al was probably overestimated by ~10% (the authors assumed that I_f was proportional to $[Cl]^{0.9}$, whereas a linear relationship between I_f and [Cl] probably held under their experimental conditions). The preferred value at 298 K was taken to be a simple mean of the four values (the value reported by Davis et al was reduced by 10%), i.e., 5.7×10^{-11}. The two values reported for E/R are in good agreement; E/R = 61 K (Manning and Kurylo) and E/R = 130 K (Lewis et al). A simple least squares fit to all the data would unfairly weight the data of Lewis et al due to the larger temperature range covered. Therefore, the preferred value of 7.7×10^{-11} exp(-90/T) is an expression which best fits the data of Lewis et al and Manning and Kurylo between 220 and 350 K.

E5.   Cl + C_3H_8. This recommendation is based on results over the temperature range 220-607 K reported in the recent discharge flow-resonance fluorescence study of Lewis et al (1980). These results are consistent with those obtained in the competitive chlorination studies of Pritchard et al (1955), Knox and Nelson (1959), Atkinson and Aschmann (1985), and Wallington et al (1988).

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E6. Cl + CH$_3$OH. This recommendation is based on the 200-500 K results of Michael et al (1979b) by the flash photolysis-resonance technique and the 298 K results of Payne et al (1987) by the discharge flow-mass spectrometry technique. Product analysis and isotopic substitution have established that the reaction mechanism consists of abstraction of a hydrogen atom from the methyl group rather than from the hydroxyl group. See Radford (1980), Radford et al (1981), Meier et al (1984), and Payne et al (1987). This reaction has been used as a source of CH$_2$OH and as a source of HO$_2$ by the reaction of CH$_2$OH with O$_2$. The results obtained in the competitive chlorination study of Wallington et al (1988) are consistent with the recommendation.

E7. Cl + CH$_3$Cl. The results reported by Clyne and Walker (1973) and Manning and Kurylo (1977) are in good agreement at 298 K. However, the value of the activation energy measured by Manning and Kurylo is significantly lower than that measured by Clyne and Walker. Both groups of workers measured the rate constant for the Cl + CH$_4$ and, similarly, the activation energy measured by Manning and Kurylo was significantly lower than that measured by Clyne and Walker. It is suggested that the discharge flow-mass spectrometric technique was in this case subject to a systematic error, and it is recommended that the flash photolysis results be used for stratospheric calculations in the 200-300 K temperature range (see discussion of the Cl + CH$_4$ studies). In the discussion of the Cl + CH$_4$ reaction it was suggested that some of the apparent discrepancy between the results of Clyne and Walker and the flash photolysis studies can be explained by nonlinear Arrhenius behavior. However, it is less likely that this can be invoked for this reaction as the pre-exponential A-factor (as measured in the flash photolysis studies) is already ~3.5 x 10^{-11} and the significant curvature which would be required in the Arrhenius plot to make the data compatible would result in an unreasonably high value for A (>2 x 10^{-10}).

E8. Cl + CH$_3$CN. The recommendation accepts the upper limit at room temperature reported by Kurylo and Knable (1984) using flash photolysis-resonance fluorescence. Poulet et al (1984a) used discharge flow-mass spectrometry and reported the expression k = 3.5 x 10^{-11} exp(-2785/T) over the temperature range 478-723 K. They also reported a room temperature value of 9 x 10^{-15}, which is a factor of 3 greater than that calculated from their expression. It appears likely that their room temperature observations were strongly influenced by heterogeneous processes. It should be noted that their extrapolated room temperature value is approximately equal to Kurylo and Knable's upper limit. Olbregts et al (1984) reported values near 400 K that agree with results of Poulet et al

E9. Cl + CH$_3$CCl$_3$. There has been only one study of this rate, that by Wine et al (1982), using a laser flash photolysis-resonance fluorescence technique. It was concluded that the presence of a reactive impurity accounted for a significant fraction of the Cl removal, and therefore only upper limits to the rate were reported for the temperature range 259-356 K. This reaction is too slow to be of any importance in atmospheric chemistry.

E10. Cl + H$_2$CO. The results from five of the six published studies (Michael et al (1979a), Anderson and Kurylo (1979), Niki et al (1978a), Fasano and Nogar (1981) and Poulet et al (1981)) are in good agreement at ~298 K, but ~50% greater than the value reported by Foon et al (1979). The preferred value at 298 K was obtained by combining the absolute values reported by Michael et al, Anderson and Kurylo, and Fasano and Nogar, with the values obtained by combining the ratio of k(Cl + H$_2$CO)/k(Cl + C$_2$H$_6$) reported by Niki et al (1.3±0.1) and by Poulet et al (1.16±0.12) with the preferred value of 5.7 x 10^{-11} for k(Cl + C$_2$H$_6$) at 298 K. The preferred value of E/R was obtained from a least squares fit to all the data reported in Michael et al and in Anderson and Kurylo. The A-factor was adjusted to yield the preferred value at 298 K.

E11. Cl + H$_2$O$_2$. The absolute rate coefficients determined at ~298 K by Watson et al (1976), Leu and DeMore (1976), Michael et al (1977), Poulet et al (1978a) and Keyser (1980a) range in value from (3.6-6.2) x 10^{-13}. The studies of Michael et al, Keyser, and Poulet et al are presently considered to be the most reliable. The preferred value for the Arrhenius expression is taken to be that

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reported by Keyser. The A-factor reported by Michael et al is considerably lower than that expected from theoretical considerations and may possibly be attributed to decomposition of H_2O_2 at temperatures above 300 K. The data of Michael et al at and below 300 K are in good agreement with the Arrhenius expression reported by Keyser. More data are required before the Arrhenius parameters can be considered to be well established. Heneghan and Benson (1983), using mass spectrometry, confirmed that this reaction proceeds only by the abstraction mechanism giving HCl and HO_2 as products.

E12. **Cl + HOCl.** This recommendation is based on results over the temperature range 243-365 K using the discharge flow-mass spectrometric technique in the only reported study of this rate, Cook et al (1981a). Ennis and Birks (1985) have measured the product distribution in a discharge flow-mass spectrometric system and found that the major reaction channel is that to give the products Cl_2 + OH with a yield of 91±6%.

E13. **Cl + HNO₃.** The recommended upper limit at room temperature is that reported in the recent study of Wine et al (1988), in which long path laser absorption spectroscopy was used to look for the appearance of NO_3 following the pulsed laser photolysis of Cl_2-HNO_3 mixtures and no evidence for NO_3 production was observed. In the same study a less sensitive upper limit was derived from monitoring Cl atom decay by resonance fluorescence. A less sensitive upper limit was also found in the recent discharge flow-EPR study of Zagogianni et al (1987). Higher values obtained in earlier studies (Leu and DeMore (1976), Kurylo et al (1983b), and Clark et al (1982)) as well as the higher temperature results of Poulet et al (1978a) are not used.

E14. **Cl + HO₂.** The recommendations for the two reaction channels are based upon the results by Lee and Howard (1982) using a discharge flow system with laser magnetic resonance detection of HO_2, OH and ClO. The total rate constant is temperature independent with a value of (4.2±0.7) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} over the temperature range 250-420 K. This value for the total rate constant is in agreement with the results of indirect studies relative to Cl + H_2O_2 (Leu and DeMore (1976), Poulet et al (1978a), Burrows et al (1979)) or to Cl + H_2 (Cox (1980)). The contribution of the reaction channel producing OH + ClO (21% at room temperature) is much higher than the upper limit reported by Burrows et al (1% of total reaction). Cattell and Cox (1986) using a molecular modulation-UV absorption technique over the pressure range 50-760 torr report results in good agreement with those of Lee and Howard both for the overall rate constant and for the relative contribution of the two reaction channels. The rate constant for the channel producing ClO + OH can be combined with that for the reaction ClO + OH > Cl + HO_2 to give an equilibrium constant from which a value of the heat of formation of HO_2 at 298 K of 3.0 kcal/mol can be derived.

E15. **Cl + Cl₂O.** The preferred value was determined from two independent absolute rate coefficient studies reported by Ray et al (1980), using the discharge flow-resonance fluorescence and discharge flow-mass spectrometric techniques. This value has been confirmed by Burrows and Cox (1981) who determined the ratio k(Cl + Cl_2O)/k(Cl + H_2) = 6900 in modulated photolysis experiments. The earlier value reported by Basco and Dogra (1971a) has been rejected. The Arrhenius parameters have not been experimentally determined; however, the high value of k at 298 K precludes a substantial positive activation energy.

E16. **Cl + OClO.** The recent data of Toohey (1988) are in good agreement with the results of Bemand et al (1973) at room temperature, and the recommended value at room temperature is the mean of the values reported in these two studies. The slight negative temperature dependence reported by Toohey (1988) is accepted but with error limits that encompass the temperature independence reported in the earlier study.

E17. **Cl + ClOO.** Values of 1.56 x 10^{-10}, 9.8 x 10^{-11}, and 1.67 x 10^{-10} have been reported for k_a(Cl + ClOO → Cl_2 + O_2) by Johnston et al (1969), Cox et al (1979), and Ashford et al (1978), respec-

tively. Values of 108, 20.9, 17, and 15 have been reported for $k_a(Cl + ClOO \rightarrow Cl_2 + O_2)/k(Cl + ClOO \rightarrow 2\ ClO)$ by Johnston et al, Cox et al, Ashford et al, and Nicholas and Norrish (1968). Obviously the value of 108 by Johnston et al is not consistent with the others, and the preferred value of 17.6 was obtained by averaging the other three values (this is in agreement with a value that can be derived from a study by Porter and Wright (1953)). The absolute values of k_a and k_b are dependent upon the choice of ΔH_f^o (ClOO) (the values of ΔH_f^o (ClOO) reported by Cox et al and Ashford et al are in excellent agreement, i.e. 22.7 and 22.5 kcal/mol, respectively). The preferred value of $k_a(Cl + ClOO \rightarrow Cl_2 + O_2)$ is taken to be the average of the three reported values, i.e. 1.4×10^{-10} cm^3 molecule^{-1} s^{-1}. Consequently, the preferred value of $k_b(Cl + ClOO \rightarrow 2\ ClO)$ is $k_a/17.6$, i.e. 8.0×10^{-12} cm^3 molecule^{-1} s^{-1}. The E/R values are estimated to be zero, which is consistent with other experimentally determined E/R values for atom-radical reactions.

E18. $Cl + Cl_2O_2$. New Entry. The recommended value is that determined by Friedl (private communication, 1989) in a study using a DF-MS technique. It is in agreement with the value reported by Cox and Hayman (1988) in a study using a static photolysis technique with photodiode array UV spectroscopy.

E19. $Cl + ClONO_2$. Flash photolysis/resonance fluorescence studies by Margitan (1983a) and by Kurylo et al (1983a), which are in good agreement, show that the rate constant for this reaction is almost two orders of magnitude faster than that indicated by the previous work of Kurylo and Manning (1977) and Ravishankara et al (1977b). It is probable that the slower reaction observed by Kurylo and Manning was actually $O + ClNO_3$, not $Cl + ClNO_3$. The preferred value averages the results of the two new studies.

E20. $Cl + NO_3$. The recommended value at room temperature is based on the recent discharge flow-EPR study of Mellouki et al (1987). The results of this direct absolute rate study are preferred over results of the earlier relative rate studies of Cox et al (1984a), Burrows et al (1985b), and Cox et al (1987), in all of which NO_3 was monitored in the photolysis of $Cl_2-ClONO_2-N_2$ mixtures. Complications in the chemistry of the earlier systems probably contributed to the spread in reported values. This radical-radical reaction is expected to have negligible temperature dependence, which is consistent with the results from the study of Cox et al (1987) in which the complications must have been temperature-independent.

E21. $Cl + N_2O$. This rate coefficient has been determined in a study of the halogen-catalyzed decomposition of nitrous oxide at about 1000 K by Kaufman et al (1956). The largest value reported was 10^{-17} cm^3 molecule^{-1} s^{-1}, with an activation energy of 34 kcal/mol. Extrapolation of these results to low temperature shows that this reaction cannot be of any significance in atmospheric chemistry.

E22. $Cl + ClNO$. Recent studies have significantly improved the data base for this rate constant. The discharge flow-resonance fluorescence study of Abbatt et al (1989) provides the first reliable data on the temperature dependence. The laser photolysis-LMR study of Chasovnikov et al (1987) provides rate data for each Cl atom spin state, and they attribute the low value reported by Nelson and Johnston (1981) in a laser flash photolysis-resonance fluorescence study to reaction of the Cl $^2P_{1/2}$ state. Adsorption and decomposition of ClNO on the walls of their static system may account for the very low value of Grimely and Houston (1980). The results of Clyne and Cruse (1972) in a discharge flow-resonance fluorescence study are significantly lower than all recent results. The recommended value at room temperature is the mean of the values reported by Abbatt et al (1989), Chasovnikov et al (1987), Nesbitt et al (1987), and Kita and Stedman (1982). The recommended temperature dependence is from the study of Abbatt et al (1989).

E23. $ClO + O$. Recently there have been five studies of this rate constant over an extended temperature range using a variety of techniques: Leu (1984b); Margitan (1984b); Schwab et al (1984); Ongstad and Birks (1986); and Nicovich et al (1988). The recommended value is based on a least squares fit to the data reported in these studies and in the earlier studies of Zahniser and Kaufman (1977)

and Ongstad and Birks (1984). Values reported in the early studies of Bemand et al (1973) and Clyne and Nip (1976b) are significantly higher and were not used in deriving the recommended value. Leu and Yung (1987) were unable to detect $O_2('\Sigma)$ or $O_2('\Delta)$ and set upper limits to the branching ratios for their production of 4.4×10^{-4} and 2.5×10^{-2}.

E24. ClO + NO. The absolute rate coefficients determined in the four discharge flow-mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978), Ray and Watson (1981a) and Clyne and MacRobert (1980)) and the discharge flow laser magnetic resonance study Lee et al (1982) are in excellent agreement at 298 K, and are averaged to yield the preferred value. The value reported by Zahniser and Kaufman (1977) from a competitive study is not used in the derivation of the preferred value as it is about 33% higher. The magnitudes of the temperature dependences reported by Leu and DeMore (1978) and Lee et al are in excellent agreement. Although the E/R value reported by Zahniser and Kaufman (1977) is in fair agreement with the other values, it is not considered as it is dependent upon the E/R value assumed for the Cl + O_3 reaction. The Arrhenius expression was derived from a least squares fit to the data reported by Clyne and Watson, Leu and DeMore, Ray and Watson, Clyne and MacRobert and Lee et al.

E25. ClO + NO_3. The recommended value is based on results reported by Cox et al (1984a) and by Cox et al (1987) in the only reported studies of this reaction. Both studies used the modulated photolysis of Cl_2 + $ClONO_2$ mixtures. In the new study a small temperature dependence is reported, but because of uncertainties in the data a temperature-independent value is recommended in this evaluation.

E26. ClO + HO_2. There have now been five studies of this rate constant. Three were low pressure discharge flow studies, each using a different experimental detection technique (Reimann and Kaufman, 1978; Stimpfle et al, 1979; Leck et al, 1980), and two were molecular modulation studies; at one atmosphere (Burrows and Cox, 1981), and over the pressure range 50-760 torr (Cattell and Cox, 1986). The 298 K values reported, in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, are: 3.8 ± 0.5 (Reimann and Kaufman), 6.3 ± 1.3 (Stimpfle et al), 4.5 ± 0.9 (Leck et al), 5.4 (Burrows and Cox), and 6.2 ± 1.5 (Cattell and Cox). The recommended value is the mean of these values. The study of Cattell and Cox over an extended pressure range when combined with results of the low pressure discharge flow studies seem to indicate that this reaction exhibits no pressure dependence at room temperature. The only temperature dependence study (Stimpfle et al) resulted in a non-linear Arrhenius behavior. The data were best described by a four parameter equation of the form $k = Ae^{-B/T} + CT^n$, possibly suggesting that two different mechanisms may be occurring. The expression forwarded by Stimpfle et al was $3.3 \times 10^{-11}exp(-850/T) + 4.5 \times 10^{-12} (T/300)^{-3.7}$. Two possible preferred values can be suggested for the temperature dependence of k; (a) an expression of the form suggested by Stimpfle et al, but where the values of A and C are adjusted to yield a value of 5.0×10^{-12} at 298 K, or (b) a simple Arrhenius expression which fits the data obtained at and below 300 K (normalized to 5.0×10^{-12} at 298 K). The latter form is preferred. The two most probable pairs of reaction products are, (1) HOCl + O_2 and (2) HCl + O_3. Leu (1980b) and Leck et al used mass spectrometric detection of ozone to place upper limits of 1.5% (298 K) and 3.0% (248 K); and 2.0% (298 K), respectively, on k_2/k. Burrows and Cox report an upper limit of 0.3% for k_2/k at 300 K.

E27. ClO + H_2CO. Poulet et al (1980) have reported an upper limit of 10^{-15} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K using the discharge flow-EPR technique.

E28. ClO + OH. The recommended value is based on a fit to the 219-373 K data of Hills and Howard (1984), the 243-298 K data of Burrows et al (1984a), and the 298 K data of Poulet et al (1986a). Data reported in the studies of Ravishankara et al (1983a), and Leu and Lin (1979) were not used in deriving the recommended value because in these studies the concentration of ClO was not determined directly. The results of Burrows et al are temperature-independent while those of Hills and Howard

show a slight negative temperature dependence. The fraction of total reaction yielding HO_2 + Cl as products has been determined by Leu and Lin (>0.65); Burrows et al (0.85±0.2); Hills and Howard (0.86±0.14); and Poulet et al (0.98±0.12). The latest study gives an upper limit of 0.14 for the branching ratio to give HCl + O_2 as products. The uncertainties in all studies allow for the possibility that the HCl yield is indeed zero.

E29. ClO Reactions. These upper limits are based on the data of Walker (reported in Clyne and Watson, 1974a). The upper limits shown for k(298) were actually determined from data collected at either 587 or 670 K. The Arrhenius expressions were estimated based on this ~600 K data.

E30. ClO + ClO. There are three bimolecular channels for this reaction: ClO + ClO → OClO + Cl (k_1); ClO + ClO → Cl + ClOO (k_2); and ClO + ClO → Cl_2 + O_2 (k_3). The recommended values given here are for the total rate coefficient at low pressures. They are based largely on results obtained in the discharge flow studies of Clyne and co-workers as discussed in the reviews by Watson (1977, 1980). Note that the rate constant is here defined as $-d(ClO)/dt = 2 k (ClO)^2$. Molecular modulation studies such as those of Cox and co-workers (see Hayman et al., 1986) have given a similar temperature dependence but somewhat lower rate constant values. The product branching ratios and their dependence on temperature and pressure are not well established. The low pressure results indicate that k_2 and k_3 are both important, while k_1 represents only about 10 percent of the total reaction. The reaction exhibits both bimolecular and termolecular reaction channels (see entry for this reaction in Table 2). The termolecular reaction, presumably to give the dimer, dominates at pressures higher than about 10 torr; however, the role of the dimer in the overall reaction is unclear - whether it is merely in equilibrium with ClO or decomposes to give the same products given in the bimolecular reaction channels. Some product branching ratio data have been derived from studies of the chlorine photosensitized decomposition of ozone. In these systems there are uncertainties concerning the need for some reaction of the Cl_2O_2 complex in order to account for the strong temperature dependence of the ozone quantum yield and also concerning the possible role of ClO complex formation with O_2 and subsequent reactions of the $ClO-O_2$ complex. The equilibrium constant for formation of the Cl_2O_2 dimer is given in Table 3.

E31. ClO + O_3. The branching ratio between the two possible channels is not known, but, for the present discussion, is assumed to be unity. There is no evidence that either reaction actually occurs. The Arrhenius parameters were estimated, and the upper limit rate constants are based on data reported by DeMore, Lin and Jaffe (1976) and by Wongdontri-Stuper et al (1979).

E32. ClO + CH_3O_2. New Entry. There has been no direct study of this reaction. Simon et al (1989) studied the modulated photolysis of $Cl_2/CH_4/Cl_2O/O_2$ mixtures using UV-VIS and FTIR absorption spectroscopy. ClO was monitored at 292 nm and CH_3O_2 at 240 nm. The authors state that the observations were best explained by postulating a fast bimolecular reaction between these species. They fitted the absorption data to a chemical model and thereby derived a value for the rate constant of 3 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K. The evidence for reaction is extremely indirect, and the derived results must be regarded as highly uncertain. The authors interpret their results as indicating that the products are ClOO and CH_3O.

E33. OH + Cl_2. The recommended room temperature value is the average of the results reported by Boodaghians et al (1987), Loewenstein and Anderson (1984), Ravishankara et al (1983a), and Leu and Lin (1979). The temperature dependence is from Boodaghians et al Loewenstein and Anderson determined that the exclusive products are Cl + HOCl.

E34. OH + HCl. The recommended value is based on a least squares fit to the data reported in the recent studies by Molina et al (1984), Keyser (1984), and Ravishankara et al (1985b). In these studies particular attention was paid to the determination of the absolute concentration of HCl by UV and IR spectrophotometry. Earlier studies by Takacs and Glass (1973c), Zahniser et al (1974), Smith and

Zellner (1974), Ravishankara et al (1977a), Hack et al (1977), Husain et al (1981), Cannon et al (1984), Husain et al (1984), and Smith and Williams (1986) had reported somewhat lower room temperature values.

E35.   OH + HOCl. In the only reported study of this system Ennis and Birks (1988) reported the value of this rate constant at room temperature to lie in the range $(1.7 - 9.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. A temperature dependent expression has been estimated by choosing a pre-exponential factor by analogy with the OH + H$_2$O$_2$ reaction and selecting the midpoint of the experimental range for the room temperature rate constant. The large uncertainty factor is needed to encompass the entire range.

E36.   OH + CH$_3$Cl. The preferred values were obtained using only absolute rate coefficient data. The data of Howard and Evenson (1976a), Davis et al (1976), Perry et al (1976a), Paraskevopoulos et al (1981) and Jeong and Kaufman (1982) are in good agreement and were used to determine the preferred values. The preferred Arrhenius expression was derived from a least squares fit to the data below 400 K. Results of a new study by Taylor et al (1989) over the temperature range 295-800 K are in good agreement with the recommendation at room temperature, but values extrapolated to stratospheric temperatures are substantially lower than the recommendation.

E37.   OH + CH$_2$Cl$_2$. The data of Howard and Evenson (1976a), Perry et al (1976), Davis et al (1976) and Jeong and Kaufman (1982) are in reasonable agreement. The temperature dependence data of Davis et al tend to somewhat smaller values than Jeong and Kaufman but the resulting activation energies are in good agreement. The preferred Arrhenius expression was derived from a least squares fit to the data below 400 K. The recommended room temperature value was derived from the Arrhenius expression at 298 K. Results of a new study by Taylor et al (1989) over the temperature range 298-775 K are in reasonable agreement with the recommendation at room temperature and when extrapolated to stratospheric temperatures.

E38.   OH + CHCl$_3$. The preferred values were obtained using only absolute rate coefficient data. The accuracy of the OH + CH$_4$/OH + CHCl$_3$ study (Cox et al, 1976a) was probably no better than a factor of 2. The data of Howard and Evenson (1976a), Davis et al (1976) and Jeong and Kaufman (1982) are in good agreement and were used to determine the preferred values. The preferred Arrhenius expression was derived from a least squares fit to the data below 400 K. Results of a new study by Taylor et al (1989) over the temperature range 295-775 K are in good agreement with the recommendation at room temperature, but values extrapolated to stratospheric temperatures are higher than the recommendation.

E39.   OH + CHFCl$_2$. Absolute rate coefficient data for this reaction have been reported by Howard and Evenson (1976a), Perry et al (1976a), Watson et al (1977), Chang and Kaufman (1977a), Clyne and Holt (1979b), Paraskevopoulos et al (1981) and Jeong and Kaufman (1982). The data base is well established and there have been no new data recently. The preferred values are derived from a fit to all data below 400 K except the rate constants of Clyne and Holt (1979b) which have a significantly larger temperature dependence than all the other studies. The rate constants from the latter study are consistently larger than those obtained in all other studies. The expression given here agrees with the recommended expression from JPL 87-41 to within about 15% over the stratospheric temperature range.

E40.   OH + CHF$_2$Cl. Absolute rate coefficient data for this reaction have been reported by Howard and Evenson (1976a), Atkinson et al (1975), Watson et al (1977), Chang and Kaufman (1977a), Handwerk and Zellner (1978), Clyne and Holt (1979b), Paraskevopoulos et al (1981) and Jeong and Kaufman (1982). The data base is well established and there have been no new data recently. The preferred values are derived from a fit to all data below 400 K except the rate constants of Clyne and Holt (1979b), which have a significantly larger temperature dependence than all the other studies. The expression given here agrees with the recommended expression from JPL 87-41 to within about 15% over the stratospheric temperature range.

E41. OH + CH$_2$FCl. The data for this reaction are in excellent agreement. The recommended Arrhenius expression was derived from the room temperature data of Howard and Evenson (1976a) and Paraskevopoulos et al (1981), and the temperature dependence data of Watson et al (1977), Handwerk and Zellner (1978) and Jeong and Kaufman (1982) below 400 K. The expression given here agrees with the recommended expression from JPL 87-41 to within about 15% over the stratospheric temperature range.

E42. OH + CH$_3$CCl$_3$. This evaluation is based on the data of Jeong and Kaufman (1979) and Kurylo et al (1979). Their results are in excellent agreement over the temperature range 250-460 K. The earlier results of Howard and Evenson (1976b), Watson et al (1977), Chang and Kaufman (1977a) and Clyne and Holt (1979a) were discounted in favor of the newer results. The earlier results showed higher values of the rate constant, and lower E/R values. This may indicate that the CH$_3$CCl$_3$ used in the early studies was contaminated with small amounts of a reactive olefinic impurity.

E43. OH + CHCl$_2$CF$_3$. The preferred rate expression is derived from the temperature dependence data below 400 K of Gierczak et al (1989), Liu et al (1990), Watson et al (1979b) and the room temperature data of Howard and Evenson (1976b). The recommended value of k$_{298}$ is derived from the temperature dependence expression. The data of Clyne and Holt (1979b) were not considered.

E44. OH + CHFClCF$_3$. The preferred rate expression is derived from the temperature dependence data of Watson et al (1979b) and the room temperature data of Howard and Evenson (1976b). The recommended value of k$_{298}$ is derived from the temperature dependence expression.

E45. OH + CH$_2$ClCF$_2$Cl. The recommended temperature dependence was derived from the data of Watson et al (1979b) which were corrected by these authors for the presence of alkene impurities. The data of Jeong et al (1984), indicating substantially faster rate constants may have been affected by such impurities and hence were not included in deriving the recommendation. The preferred value of k$_{298}$ was derived from the recommended Arrhenius expression. This recommendation is essentially identical to the one in JPL 87-41.

E46. OH + CH$_2$ClCF$_3$. New Entry. The temperature dependence of the preferred rate expression was derived from the data of Handwerk and Zellner (1978). The recommended value of k$_{298}$ is the average of the values of Howard and Evenson (1975b) and Handwerk and Zellner (1978) adjusted to 298 K. The data of Clyne and Holt (1979b) were not used in deriving this recommendation.

E47. OH + CH$_3$CFCl$_2$. The preferred rate expression is significantly different from that estimated in NASA (1987) due to the recent availability of kinetics data from Gierczak et al (1989) and Liu et al (1990). There is noticeable curvature in the Arrhenius plots from both studies. While the data can be fit to a reasonably straight line over the temperature range 240-400 K, a temperature range for the fit of 273-400 K was adopted. The reaction rate at the lowest temperature, being so slow, is most likely to be affected by impurities. In addition, inclusion of the lowest temperature points in the fit results in an unusually small A-factor. Rate constants derived from this recommendation are a factor of 1-3 times larger than those from JPL 87-41 at low temperatures.

E48. OH + CH$_3$CF$_2$Cl. The recommended rate expression is derived from a fit to the temperature dependence data of Gierczak et al (1989), Liu et al (1990), Watson et al (1977) and Handwerk and Zellner (1978), and the room temperature data of Howard and Evenson (1976b), and Parakevopoulos et al (1981). The value of k$_{298}$ was derived from the rate expression. The preferred rate expression results in rate constants that are up to 25% larger at stratospheric temperatures than those derived from the JPL 87-41 recommendation.

E49.	OH + C$_2$Cl$_4$.	The preferred value at 298 K is a mean of the values reported by Howard (1976) and Chang and Kaufman (1977a). The value reported by Winer et al (1976), which is more than a factor of 10 greater, is rejected. The preferred Arrhenius parameters are those of Chang and Kaufman.

E50.	OH + C$_2$HCl$_3$.	The preferred value at 298 K is a mean of the values reported by Howard (1976) and Chang and Kaufman (1977a). The value derived from a relative rate coefficient study by Winer et al (1976) is a factor of ~2 greater than the other values and is not considered in deriving the preferred value at 298 K. The Arrhenius parameters are based on those reported by Chang and Kaufman (the A-factor is reduced to yield the preferred value at 298 K).

E51.	OH + CCl$_4$.	New Entry. The recommended upper limit at room temperature is based on the upper limit reported in the competititve study by Cox et al (1976a). The value given there has been increased by a factor of four to allow for uncertainties in the number of NO molecules oxidized. The recommendation is compatible with the less sensitive upper limits reported by Howard and Evenson (1976a) and Clyne and Holt (1979a). None of these investigators reported any evidence for reaction between these species. The A-factor was estimated and a lower limit for E/R was derived.

E52.	OH + CFCl$_3$ and OH + CF$_2$Cl$_2$.	The A-factor was estimated, and a lower limit was derived for E/R by using the upper limits reported for the rate constants by Chang and Kaufman (1977b) at about ~480 K. These expressions are quite compatible with the upper limits reported for these rate constants by Atkinson et al (1975), Howard and Evenson (1976a), Cox et al (1976a) and Clyne and Holt (1979b). None of the investigators reported any evidence for reaction between OH and these chlorofluoromethanes.

E53.	OH + ClONO$_2$.	The results reported by Zahniser et al (1977) and Ravishankara et al (1977b) are in good agreement at ~245 K (within 25%), considering the difficulties associated with handling ClONO$_2$. The preferred value is that of Zahniser et al Neither study reported any data on the reaction products.

E54.	O + HCl.	Fair agreement exists between the results of Brown and Smith (1975), Wong and Belles (1971), Ravishankara et al (1977a), Hack et al (1977) and Singleton and Cvetanovic (1981) at 300 K (some of the values for k(300 K) were obtained by extrapolation of the experimentally determined Arrhenius expressions), but these are a factor of ~7 lower than that of Balakhnin et al (1971). Unfortunately, the values reported for E/R are in complete disagreement, ranging from 2260-3755 K. The preferred value was based on the results reported by Brown and Smith, Wong and Belles, Ravishankara et al, Hack et al and Singleton and Cvetanovic but not those reported by Balakhnin et al.

E55.	O + HOCl.	There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds.

E56.	O + ClONO$_2$.	The results reported by Molina et al (1977b) and Kurylo (1977) are in good agreement, and this data has been used to derive the preferred Arrhenius expression. The value reported by Ravishankara et al (1977b) at 245 K is a factor of 2 greater than those from the other studies, and this may possibly be attributed to (a) secondary kinetic complications, (b) presence of NO$_2$ as a reactive impurity in the ClONO$_2$, or (c) formation of reactive photolytic products. None of the studies reported identification of the reaction products. The room temperature result of Adler-Golden and Wiesenfeld (1981) is in good agreement with the recommended value.

E57.	O + Cl$_2$O.	The recommendation averages the results of Miziolek and Molina (1978) for 236-295 K with the approximately 30 percent lower values of Wecker et al (1982) over the same temperature range. Earlier results by Basco and Dogra (1971c) and Freeman and Phillips (1968) have not been included in the derivation of the preferred value due to data analysis difficulties in both studies.

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E58. OClO + O. The Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

E59. OClO + O_3. New Entry. The recommended value is based on results over the temperature range 262-296 K reported by Wongdontri-Stuper et al (1979). Within the indicated uncertainty limits it also encompasses the the somewhat lower room-temperature result of Birks et al (1977).

E60. OClO + OH. New Entry. The recommended value is that reported by Poulet et al (1986b), the only reported study of this rate constant, using a discharge flow system in which OH decay was measured by LIF or EPR over the temperature range 293-473 K. Product HOCl was detected by modulated molecular beam mass spectrometry. The branching ratio for the channel to produce HOCl + O_2 was determined to be close to unity, but experimental uncertainty would allow it to be as low as 0.80.

E61. OClO + NO. The Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

E62. Cl_2O_2 + O_3. New Entry. The recommended upper limit is that determined by DeMore (private communication, 1989). It refers to a temperature of 195 K and while the reaction possibly could be faster at higher temperatures, the value of the rate at the higher temperatures would be of no significance because of the thermal decomposition of the dimer.

E63. Cl_2O_2 + NO. New Entry. The recommended upper limit determined by Friedl (private communication, 1989) in a study using a DF-MS technique.

E64. HCl + NO_3. New Entry. The recommended upper limit is that reported by Mellouki et al (1989) in a study using DF-EPR techniques. This upper limit shows that this reaction is of negligible importance in stratospheric chemistry.

E65. HCl + $ClONO_2$. Recently, results of four studies of the kinetics of this system have been published, in which the following upper limits to the homogeneous bimolecular rate constant were reported: 1×10^{-19} cm^3 molecule^{-1} s^{-1} by a static wall-less long-path UV absorption technique and a steady-state flow FTIR technique (Molina et al, 1985); 5×10^{-18} using a flow reactor with FTIR analysis (Friedl et al, 1986); and 8.4×10^{-21} using a static photolysis system with FTIR analysis (Hatakeyama and Leu, 1986 and Leu et al, 1989), and 1.5×10^{-19} by FTIR analysis of the decay of $ClONO_2$ in the presence of HCl in large-volume (2500 and 5800 liters) Teflon or Teflon-coated chambers (Atkinson et al, 1987). Earlier, Birks et al (1977) had reported a higher upper limit. All studies found this reaction to be catalyzed by surfaces. The differences in the reported upper limits can be accounted for in terms of the very different reactor characteristics and detection sensitivities of the various studies. The homogeneous reaction is too slow to have any significant effect on atmospheric chemistry.

E66. HCl + HO_2NO_2. This upper limit is based on results of static photolysis-FTIR experiments reported by Leu et al (1989).

E67. H_2O + $ClONO_2$. This recommendation is based on the upper limits to the homogeneous bimolecular rate constant reported by Atkinson et al (1986), and by Hatakeyama and Leu (1986, 1989). Atkinson et al observed by FTIR analysis the decay of $ClONO_2$ in the presence of H_2O in large-volume (2500 and 5800 liters) Teflon or Teflon-coated chambers. Their observed decay rate gives an upper limit to the homogeneous gas phase rate constant, and they conclude that the decay observed is due to heterogeneous processes. Hatakeyama and Leu, using a static photolysis system with FTIR analysis, derive a similar upper limit. Rowland et al (1986) concluded that the decay they observed resulted from rapid heterogeneous processes. The homogeneous reaction is too slow to have any significant effect on atmospheric chemistry.

E68. CX_3O_2 + NO. These recommended values for the reactions of NO with the perhalogenated methylperoxy radicals are based on the results reported by Dognon et al (1985) for the temperature range 230-430 K. They are in good agreement with the room temperature values reported for the reaction of $CFCl_2O_2$ (Lesclaux and Caralp, 1984), and CCl_3O_2 (Ryan and Plumb, 1984). Dognon et al have shown that NO_2 is the major product in these reactions.

F1. Br + O_3. The results reported for k(298 K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael et al (1978), Michael and Payne (1979), and Toohey et al (1987b) are in excellent agreement. The preferred value at 298 K is derived by taking a simple mean of these five values. The temperature dependences reported for k by Leu and DeMore and by Toohey et al are in good agreement, but they can only be considered to be in fair agreement with those reported by Michael et al and Michael and Payne. The preferred value was synthesized to best fit all the data reported from these five studies. The new results of Nicovich et al (1989) are in excellent agreement with this recommendation.

F2. Br + H_2O_2. The recommended upper limit to the value of the rate constant at room temperature is based on results reported in the recent study by Toohey et al (1987a) using a discharge flow-laser magnetic resonance technique. Their upper limit determined over the temperature range 298-378 K is consistent with less sensitive upper limits determined by Leu (1980a) and Posey et al (1981) using the discharge flow-mass spectrometric technique. The much higher value reported by Heneghan and Benson (1983) may result from the presence of excited Br atoms in the very low pressure reactor. The pre-exponential factor was chosen to be consistent with that for the Cl + H_2O_2 rate constant, and the E/R value was fitted to the upper limit at 298 K.

F3. Br + H_2CO. There have been two studies of this rate constant as a function of temperature; Nava et al (1981), using the flash photolysis-resonance fluorescence technique, and Poulet et al (1981), using the discharge flow-mass spectrometric technique. These results are in reasonably good agreement. The Arrhenius expression was derived from a least squares fit to the data reported in these two studies. The higher room temperature value of Le Bras et al (1980) using the discharge flow-EPR technique has been shown to be in error due to secondary chemistry (Poulet et al).

F4. Br + HO_2. This recommendation is based on results obtained over the 260-390 K temperature range in the recent study by Toohey et al (1987a), using a discharge flow system with LMR detection of HO_2 decay in excess Br. The room temperature value reported in this study is a factor of three higher than that reported by Poulet et al (1984b) using LIF and MS techniques and is an order of magnitude larger than the value of Posey et al (1981). The uncertainty in E/R is set to encompass the value E/R = 0, as for other radical-radical reactions. A new value determined by Le Bras (private communication, 1989) using DF-EPR techniques is in good agreement with this recommendation. The reactions of Br atoms with H_2O_2, HCHO, and HO_2 are all slower than the corresponding reactions of Cl-atoms by one to two orders of magnitude.

F5. Br + Cl_2O. The recommended value is that reported by Sander and Friedl (1989). It was derived by observing the formation of ClO using long path UV absorption following the flash photolysis of a Br_2 - Cl_2O mixture.

F6. Br + OClO. New Entry. The recommended value at room temperature is the mean of the values reported by Clyne and Watson (1977) and Toohey (1988). In both studies correction for the effect of the rapid reverse reaction was required. The temperature dependence reported by Toohey (1988) is accepted but with increased error limits.

F7. Br + Cl_2O_2. New Entry. The recommended value is that determined by Friedl (private communication, 1989) in a study using a DF-MS technique.

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F8. BrO + O. The preferred value is based on the value reported by Clyne et al (1976). This value appears to be quite reasonable in light of the known reactivity of ClO radicals with atomic oxygen. The temperature dependence k is expected to be small for an atom-radical process, e.g., O + ClO.

F9. BrO + ClO. There has recently been a substantial improvement in the database for this rate coefficient. Friedl and Sander (1989) using DF/MS techniques measured the overall rate constant over the temperature range 220-400 K and also over this temperature range determined directly branching ratios for the reaction channels producing BrCl and OClO. The same authors in a separate study using flash photolysis-ultraviolet absorption techniques (Sander and Friedl, 1989) determined the overall rate constant over the temperature range 220-400 K and pressure range 50-750 torr and also determined at 220 K and 298 K the branching ratio for OClO production. The results by these two independent techniques are in excellent agreement, with the overall rate constant showing a negative temperature dependence. Toohey and Anderson (1988) using DF/RF/LMR techniques reported room temperature values of the overall rate constant and the branching ratio for OClO production. They also found evidence for the direct production of BrCl in a vibrationally excited π state. Poulet et al (1990) using DF/MS techniques reported room temperature values of the overall rate constant and branching ratios for OClO and BrCl production. All the above mentioned results are in reasonably good agreement. Hills et al (1987, 1988) using DF/MS techniques reported an overall rate constant which was independent of temperature over the range 241-308 K and about 40 percent lower than the room temperature average of the above mentioned studies; they also determined branching ratios and and reported no BrCl production. Overall room temperature rate constant values reported also include that from the DF/MS study of Clyne and Watson (1977) and the very low value derived in the flash photolysis study of Basco and Dogra (1971b) using a different interpretation of the reaction mechanism. The most comprehensive set of branching ratio data and rate constant data is that reported by Friedl and Sander (1989). These data are supported by the results of the other more limited studies. The recommended expressions for the individual reaction channels are taken from this study. They are consistent with the entire body of data from all the studies of this reaction with the exception of the study of Hills et al and the study of Basco and Dogra.

F10. BrO + NO. The results of the three low pressure mass spectrometric studies (Clyne and Watson, 1975; Ray and Watson, 1981a; Leu, 1979a) and the high pressure uv absorption study (Watson et al, 1979a), which all used pseudo first-order conditions, are in excellent agreement at 298 K, and are thought to be much more reliable than the earlier low pressure uv absorption study (Clyne and Cruse, 1970b). The results of the two temperature dependence studies are in good agreement and both show a small negative temperature dependence. The preferred Arrhenius expression was derived from a least squares fit to all the data reported in the four recent studies. By combining the data reported by Watson et al with that from the three mass spectrometric studies, it can be shown that this reaction does not exhibit any observable pressure dependence between 1 and 700 torr total pressure. The temperature dependences of k for the analogous ClO and HO_2 reactions are also negative, and are similar in magnitude.

F11. BrO + BrO. There are two possible bimolecular channels for this reaction: BrO + BrO → 2Br + O_2 (k_1) and BrO + BrO → Br_2 + O_2 (k_2). The total rate constant for disappearance of BrO (k = k_1 + k_2) has been studied by a variety of techniques, including discharge flow-ultraviolet absorption (Clyne and Cruse, 1970a), discharge flow-mass spectrometry (Clyne and Watson, 1975) and flash photolysis-ultraviolet absorption (Basco and Dogra, 1971b; Sander and Watson, 1981b). Since this reaction is second order in [BrO], those studies monitoring [BrO] by ultraviolet absorption required the value of the cross section σ to determine k. There is substantial disagreement in the reported values of σ. Although the magnitude of σ is dependent upon the particular spectral transition selected and instrumental parameters such as spectral bandwidth, the most likely explanation for the large differences in the reported values of σ is that the techniques (based on reaction stoichiometries) used to determine σ in the early studies were used incorrectly (see discussion by Clyne and Watson).

The study of Sander and Watson used totally independent methods to determine the values of σ and (σ/k). The recommendations for k_1 and k_2 are consistent with a recommendation of $k = 1.14 \times 10^{-12}$ exp$(+255/T)$ cm^3 molecule^{-1} s^{-1}. This temperature dependence is the corrected value from Sander and Watson, and the pre-exponential factor has been chosen to fit the value of k(298 K) = 2.7×10^{-12} cm^3 molecule^{-1} s^{-1}, which is the average of the values reported by Clyne and Watson (the mass spectrometric study where knowledge of σ is not required) and by Sander and Watson (the latest absorption study). There was no observable pressure dependence from 50 to 475 torr in the latter study. Cox et al (1982) used the molecular modulation technique with ultraviolet absorption to derive a temperature independent value of k_2 which is 50 percent greater than the 298 K value recommended here.

The partitioning of the total rate constant into its two components, k_1 and k_2, has been measured by Sander and Watson at 298 K, by Jaffe and Mainquist (1980) from 258 to 333 K, and by Cox et al (1982) from 278 to 348 K. All are in agreement that $k_1/k = 0.84\pm0.03$ at 298 K. In the temperature dependent studies the quantum yield for the bromine photosensitized decomposition of ozone was measured. Jaffe and Mainquist observed a strong, unexplained dependence of the quantum yield at 298 K on [Br$_2$], and their results were obtained at much higher [Br$_2$] values than were those of Cox et al This makes a comparison of results difficult. From an analysis of both sets of temperature dependent data, the following expressions for k_1/k were derived: 0.98 exp$(-44/T)$ (Jaffe and Mainquist); 1.42 exp$(-163/T)$ (Cox et al); and 1.18 exp$(-104/T)$ (mean value). This mean value has been combined with the expression for k_1 shown in the table. The expression for k_2 results from the numerical values of k_2 at 200 K and 300 K derived from the evaluation of these expressions for k_1 and for k=$(k_1 + k_2)$.

F12. BrO + O$_3$. Based on a study reported by Sander and Watson (1981b). Clyne and Cruse (1970a) reported an upper limit of 8×10^{-14} cm^3 molecule^{-1} s^{-1} for this reaction. Both studies reported that there is no evidence for this reaction. The analogous ClO reaction has a rate constant of $<10^{-18}$ cm^3 molecule^{-1} s^{-1}.

F13. BrO + HO$_2$. The preferred value is based on the value of k(ClO + HO$_2$). Cox and Sheppard (1982) have studied the rate of this reaction in an investigation of the photolysis of O$_3$ in the presence of Br$_2$, H$_2$, and O$_2$ using the molecular modulation-ultraviolet absorption technique. Although the reported value is not very precise, it does show that this reaction occurs and at a rate comparable to that for ClO + HO$_2$. By analogy with the ClO + HO$_2$ system, the products may be expected to be HOBr + O$_2$.

F14. BrO + OH. Value chosen to be consistent with k(ClO + OH), due to the absence of any experimental data.

F15. OH + Br$_2$. The recommended room temperature value is the average of the values reported by Boodaghians et al (1987), Loewenstein and Anderson (1984), and Poulet et al (1983). The temperature independence is from Boodaghians et al. Loewenstein and Anderson determined that the exclusive products are Br + HOBr.

F16. OH + HBr. The preferred value at room temperature is the average of the values reported by Ravishankara et al (1979a) using FP-RF, by Jourdain et al (1981) using DF-EPR, and by Cannon et al (1984) using FP-LIF, and by Ravishankara et al (1985a) using LFP-RF and LFP-LIF techniques. In this latest study the HBr concentration was directly measured in-situ in the slow flow system by UV absorption. The rate constant determined in this reinvestigation is identical to the value recommended here. The data of Ravishankara et al (1979a) show no dependence on temperature over the range 249-416 K. Values reported by Takacs and Glass (1973a) and by Husain et al (1981) are a factor of two lower and were not included in the derivation of the preferred value.

F17. OH + CH$_3$Br. The recommended value is derived from a least squares fit to the data of Davis et al (1976) over the temperature range 244-350 K and the room temperature data of Howard and Evenson (1976a). The room temperature values reported in these two studies are in excellent agreement.

F18. OH + Halons. New Entry. For each of these four reactions the recommended upper limit at room temperature is the upper limit determined by Ravishankara (private communication, 1989) in a study using pulsed photolysis-LIF and DF-LMR techniques. For the reactions with CF$_2$ClBr and CF$_3$Br less sensitive upper limits were reported by Clyne and Holt (1979a) and Le Bras and Combourieu (1978) respectively.

F19. O + HBr. Results of the flash photolysis-resonance fluorescence study of Nava et al (1983) for 221-455 K and the laser flash photolysis-resonance fluorescence study of Nicovich and Wine (1989) for 250-402 K provide the only data at stratospheric temperatures. Results have also been reported by Singleton and Cvetanovic (1978) for 298-554 K by a phase-shift technique, and discharge flow results of Brown and Smith (1975) for 267-430 K and of Takacs and Glass (1973b) at 298 K. The preferred value is based on the results of Nava et al, those of Nicovich and Wine and those of Singleton and Cvetanovic over the same temperature range, since these results are less subject to complications due to secondary chemistry than are the results using discharge flow techniques. The uncertainty at 298 K has been set to encompass these latter results.

F20. NO$_3$ reactions. New Entry. The recommended values are those reported by Mellouki et al (1989) in a study using DF-EPR techniques. The value given for the reaction with BrO is the geometric mean of the reported lower and upper limits. The upper limit reported for the reaction with HBr shows that this reaction is of negligible importance in stratospheric chemistry.

G1. F + O$_3$. The only experimental data is that reported by Wagner et al (1972). The value appears to be quite reasonable in view of the well known reactivity of atomic chlorine with O$_3$.

G2. F + H$_2$. The value of k at 298 K seems to be well established with the results reported by Zhitneva and Pshezhetskii (1978), Heidner et al (1979, 1980), Wurzberg and Houston (1980), Dodonov et al (1971), Clyne et al (1973), Bozzelli (1973), Igoshin et al (1974), Clyne and Hodgson (1985) and Stevens et al (1989) being in excellent agreement (range of k being 2.3-3.0 x 10^{-11} cm^3 molecule^{-1} s^{-1}). The preferred value at 298 K is taken to be the mean of the values reported in these references. Values of E/R range from 433-595 K (Heidner et al; Wurzberg and Houston; Igoshin et al; and Stevens et al). The preferred value of E/R is derived from a fit to the data in these studies. The A-factor was chosen to fit the recommended room temperature value.

G3. F + CH$_4$. The three absolute rate coefficients determined by Wagner et al (1971), Clyne et al (1973) and Kompa and Wanner (1972) at 298 K are in good agreement; however, this may be somewhat fortuitous as the ratios of k(F + H$_2$)/k(F + CH$_4$) determined by these same groups can only be considered to be in fair agreement, 0.23, 0.42 and 0.88. The values determined for k (298) from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 0.42 reported for k(F + H$_2$)/k(F + CH$_4$) by Foon and Reid (1971) is in good agreement with that reported by Clyne et al. Fasano and Nogar (1982) determined the absolute room temperature rate coefficient, and the rate coefficient relative to that of the reaction F + D$_2$. The preferred value for k (298) is a weighted mean of all the results. The magnitude of the temperature dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported by Wagner et al, and Foon and Reid, and the preferred Arrhenius parameters of the F + H$_2$ reaction. This reaction has been reviewed by both Foon and Kaufman (1975) and Jones and Skolnik (1976). The A-factor may be too high.

G4. F + H$_2$O. The recommended temperature-independent value is based on results reported in the recent study of Stevens et al (1989) over the temperature range 240-373 K using a discharge flow system

with chemical conversion of fluorine atoms to deuterium atoms and detection of the latter by resonance fluorescence. This value is in excellent agreement with the room temperature results of Frost et al (1986) and Walther and Wagner (1983). The latter authors in a limited temperature dependent study reported an E/R value of 400 K. Although these data have not been included in the derivation of the preferred value, with the exception of the one low temperature data point, they are encompassed within the indicated uncertainty limits.

G5. $F + HNO_3$. New Entry. The recommendation is based on results of the temperature-dependent study of Wine et al (1988) and the room temperature results of Mellouki et al (1987) and Rahman et al (1988). The values at room temperature are in good agreement. The study of Wine et al (1988) was over the temperature range 260-373 K. Below 320 K the data were fitted with the Arrhenius expression recommended here, whereas at higher temperatures a temperature-independent value was found, suggesting the occurrence of different mechanisms in the two temperature regimes.

G6. $NO + FO$. This is the value reported by Ray and Watson (1981a) for k at 298 K using the discharge flow-mass spectrometric technique. The temperature dependence of k is expected to be small for such a radical-radical reaction. The temperature dependences of k for the analogous ClO and BrO reactions (Table 1) are small and negative.

G7. $FO + FO$. The value of k(FO + FO) reported by Clyne and Watson (1974b) was obtained in a more direct manner than that of Wagner et al (1972), and as such is less susceptible to error due to the presence of complicating secondary reactions. The value recommended in this assessment is a weighted average of the two studies. From the data of Wagner et al it can be seen that the dominant reaction channel is that producing $2F + O_2$. However, their data base is not adequate to conclude that this is the only process.

G8. $FO + O_3$. The FO + O_3 reaction has two possible pathways which are exothermic, resulting in the production of $F + 2 O_2$ or $FO_2 + O_2$. Although this reaction has not been studied in a simple, direct manner, two studies of complex chemical systems have reported some kinetic information about it. Starrico et al (1962) measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, ~4600, to be due to the rapid regeneration of atomic fluorine via the FO + $O_3 \rightarrow F + 2O_2$ reaction. However, their results are probably also consistent with the chain propagation process being FO + FO $\rightarrow$ 2F + O_2 (the latter reaction has been studied twice (Wagner et al, 1972; Clyne and Watson, 1974b)), and although the value of $[F]_{produced}/[FO]_{consumed}$ is known to be close to unity, it has not been accurately determined. Consequently it is impossible to ascertain from the experimental results of Starrico et al whether or not the high quantum yields for ozone destruction should be attributed to the FO + O_3 reaction producing either $F + 2 O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner et al utilized a low pressure discharge flow-mass spectrometric system to study the $F + O_3$ and FO + FO reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the FO + O_3 reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(FO + FO) of 3 x 10^{-11} is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$, or the FO + O_3 reactions being not of negligible importance in their study. Consequently, it is not possible to determine a value for the FO + O_3 reaction rate constant from existing experimental data. It is worth noting the analogous ClO + O_3 reactions are extremely slow (<10^{-18} cm^3 molecule^{-1} s^{-1}) (DeMore et al, 1976), and upper limits of 8 x 10^{-14} (Clyne and Cruse, 1970a) and 5 x 10^{-15} cm^3 molecule^{-1} s^{-1} (Sander and Watson, 1981b) have been reported for BrO + O_3.

G9. $O + FO$. This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of FO is similar to that of ClO and BrO. The temperature dependence of the

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rate constant is expected to be small, as for the analogous ClO reaction.

G10. $O + FO_2$. No experimental data. The rate constant for such a radical-atom process is expected to approach the gas collision frequency, and is not expected to exhibit a strong temperature dependence.

G11. $OH + CHF_3$. New Entry. The recommendation is based on three data points: the room temperature points of Howard and Evenson (1976a), and the 387 K and 410 K points of Jeong and Kaufman (1982). The data of Clyne and Holt (1979b) were not considered because of the large disparity with other studies. Because of experimental complications associated with the measurement of rate constants near 10^{-16} cm^3 $molecule^{-1}$ s^{-1}, the k_{298} determinations of Howard and Evenson (1976a) and Nip et al (1979) should be considered upper limits. The Howard and Evenson value, being the smaller of the two, was therefore used as the basis for the k_{298} recommendation.

G12. $OH + CH_2F_2$. New Entry. The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982) below 400 K. The recommendation for k_{298} is derived from the average of the room temperature data of Jeong and Kaufman (1982), Howard and Evenson (1976a) and Nip et al (1979). Although the data of Clyne and Holt (1979b) are consistent with the data from the other studies, this study is not included in the least squares fit.

G13. $OH + CH_3F$. New Entry. The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982) below 400 K. The recommendation for k_{298} is derived from the average of the room temperature data of Jeong and Kaufman (1982), Howard and Evenson (1976a) and Nip et al (1979).

G14. $OH + CHF_2CF_3$. New Entry. The only temperature dependence data for this reaction are those of Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreement between the Clyne and Holt data and that of other workers for many other halomethanes and haloethanes, the Clyne and Holt data were not used. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated by analogy with the reaction of OH with CH_2FCF_3.

G15. $OH + CHF_2CHF_2$. New Entry. For the preferred rate expression, the data of Clyne and Holt (1979b) were rejected in favor of an estimated temperature dependence. The recommended value of k_{298} was obtained by adjusting the 294 K value of Clyne and Holt (1979b) to 298 K.

G16. $OH + CH_2FCF_3$. The preferred rate expression was derived from the data of Gierczak et al (1989), Liu et al (1990) and the room temperature data point of Martin and Paraskevopoulos (1983). The recommended value of k_{298} is obtained from the rate expression. The data of Clyne and Holt (1979b) were not used. With the inclusion of the new data of Gierczak et al and Liu et al this recommendation is considerably different from that of JPL 87-41, which was based primarily on the data of Jeong (1984). The newer data suggest that the latter study may have overestimated the rate constant due to the presence of reactive impurities which can perturb this relatively slow reaction. This recommendation therefore results in significantly (factor of 2-4) smaller rate constants at stratospheric temperatures.

G17. $OH + CH_2FCHF_2$. New Entry. The only temperature dependence data for this reaction are those of Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreement between the Clyne and Holt data and that of other workers for several other halomethanes and haloethanes, the Clyne and Holt data were not used in deriving this recommendation. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated.

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G18. OH + CH$_3$CF$_3$. New Entry. The only temperature dependence data for this reaction are those of Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreement between the Clyne and Holt data and that of other workers for several other halo-methanes and haloethanes, the Clyne and Holt data were not used in deriving this recommendation. The preferred value of k$_{298}$ is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated by comparison with the reaction of OH with CH$_2$FCF$_3$.

G19. OH + CH$_2$FCH$_2$F. New Entry. The preferred rate expression is derived by fitting an estimated temper-ature dependence to the room temperature data of Martin and Paraskevopoulos (1983).

G20. OH + CH$_3$CHF$_2$. Changed from 87-41. The preferred rate expression is derived from the temperature dependence data of Geirczak et al (1989) and Liu et al (1990) and the room temperature data of Howard and Evenson (1976b), Handwerk and Zellner (1978) and Nip et al (1979). The data of Clyne and Holt (1979b) were not used in this derivation. The value for k$_{298}$ is that calculated from the expression.

G21. OH + CH$_3$CH$_2$F. New Entry. There are no temperature dependence data for this reaction. The temper-ature dependence of the recommended expression was derived by analogy with members of the homologous series which includes the OH + C$_2$H$_6$ and OH + CH$_3$CHF$_2$ reactions. The value of k$_{298}$ was taken from the study of Nip et al (1979). Singleton et al (1980) determined that 85 ± 3% of the abstraction by OH is from the fluorine substituted methyl group.

G22. CF$_3$O$_2$ + NO. The recommended value for the reaction of NO with this perhalogenated methylperoxy radical is based on the results reported by Dognon et al (1985) for the temperature range 230-430 K. It is in good agreement with the room temperature value reported by Plumb and Ryan (1982a). Dognon et al have shown that NO$_2$ is the major product in this reaction.

H1. OH + H$_2$S. Changed from 87-41. The values of k(298) and E/R are taken from a composite unweighted least squares fit to the individual data points of Perry et al (1976b), Cox and Sheppard (1980), Wine et al (1981a), Leu and Smith (1982a), Michael et al (1982), Lin (1982), Lin et al (1985), Barnes et al (1986a), and Lafage et al (1987). The studies of Leu and Smith (1982a), Lin et al (1985), Lin (1982), and Lafage et al (1987) show a slight parabolic temperature dependence of k with a minimum occurring near room temperature. However, with the error limits stated in this evaluation, all data are fit reasonably well by an Arrhenius expression. Lafage et al and Michael et al discuss the results in terms of a two channel reaction scheme involving direct H atom abstraction and complex (adduct) formation. Lafage et al analyzed their results above room temperature to yield an apparent E/R = 400 K for the abstraction channel in good agreement with the E/R value determined above room temperature by Westenberg and de Haas (1973b). The results of these latter workers lie systematically higher (by about 70%), presumably due to secondary reactions.

The room temperature value of Stuhl (1974) lies just outside the 2σ error limit set for k(298).

H2. OH + OCS. The value of k(298 K) is an average of the determinations by Wahner and Ravishankara (1987) and Cheng and Lee (1986). The values determined by these authors lie a factor of three higher than the earlier room temperature measurements of Leu and Smith (1981). As discussed in the recent studies, this difference may be due to an overcorrection of the data by Leu and Smith to account for OH reaction with H$_2$S impurities and also to possible regeneration of OH. Neverthe-less, the uncertainty factor at 298 K has been set to encompass the earlier study within 2σ. The work by Wahner and Ravishankara (1987) supersedes the study of Ravishankara et al (1980b) which minimized complications due to secondary and/or excited state reactions interfering with the experiments of Atkinson et al (1978) and Kurylo (1978b). The upper limit for k(298 K) reported by Cox and Sheppard (1980) is too insensitive to permit comparison with the more recent studies. The room temperature measurements Wahner and Ravishankara demonstrate the lack of an effect of total

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pressure (or O_2 partial pressure) on the rate constant and are supported by the more limited pressure and O_2 studies of Cheng and Lee. The E/R value recommended is that of Cheng and Lee, which is considerably lower than reported by Leu and Smith, although this difference may be due in part to the earlier-mentioned overcorrection of the data by these latter authors.

Product observations by Leu and Smith indicate that SH is a primary product of this reaction and tentatively confirm the suggestion of Kurylo and Laufer (1979) that the reaction produces predominantly SH + CO_2 through a complex (adduct) mechanism (similar to the adduct formation seen in the OH + CS_2 reactions). However, the absence of an O_2/pressure effect for OH + OCS is markedly different from observations in the OH + CS_2 reaction system (see following note).

H3. OH + CS_2. There is a consensus of experimental evidence indicating that this reaction proceeds very slowly as a direct bimolecular process. Wine et al (1980) set an upper limit on k(298 K) of 1.5×10^{-15} cm^3 $molecule^{-1}$ s^{-1}. A consistent upper limit is also reported by Iyer and Rowland (1980) for the rate of direct production of OCS in this reaction system, suggesting that OCS and SH are primary products of a bimolecular process. This mechanistic interpretation is further supported by the studies of Leu and Smith (1982b) and Biermann et al (1982), which set somewhat higher upper limits on k(298 K). The more rapid reaction rates observed by Atkinson et al (1978), Kurylo (1978b), and Cox and Sheppard (1980) may be attributed to severe complications arising from excited state and secondary chemistry in their photolytic systems. The Cox and Sheppard study in particular may have been affected by the reaction of electronically excited CS_2 (produced via the 350 nm photolysis) with O_2 (in the 1 atmosphere synthetic air mix) as well as by the accelerating effect of O_2 on the OH + CS_2 reaction which has been observed by other workers and is summarized below. The importance of the electronically excited CS_2 reaction in the tropospheric oxidation of CS_2 to OCS has been discussed by Wine et al (1981d).

An accelerating effect of O_2 on the OH + CS_2 reaction rate has been observed by Jones et al (1982), Barnes et al (1983), and Hynes et al (1988), along with a near unity product yield for SO_2 and OCS. In the latter two studies, the effective bimolecular rate constant was found to be a function of total pressure ($O_2 + N_2$) as well, and exhibited an appreciable negative temperature dependence. These observations are consistent with the formation of a long-lived adduct as postulated by Kurylo (1978b) and Kurylo and Laufer (1979), followed by its reaction with O_2:

$$OH + CS_2 + M \overset{k_a}{\underset{k_b}{\rightleftarrows}} HOCS_2 + M$$

$$HOCS_2 + O_2 \overset{k_c}{\rightarrow} Products$$
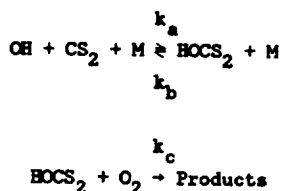
Hynes et al (1988) have, in fact, directly observed the approach to equilibrium in this reversible adduct formation. In their study, the equilibrium constant was measured as a function of temperature and the heat of formation of $HOCS_2$ calculated (-27.4 kcal/mole). A rearrangement of this adduct followed by dissociation into OCS and SH corresponds to the low k (bimolecular) channel referred to earlier. Hynes et al (1988) measure a rate constant for this process in the absence of O_2 (at approximately one atmosphere of N_2) to be < 8×10^{-16} cm^3 $molecule^{-1}$ s^{-1}. The effective second-order rate constant for CS_2 or OH removal in the above reaction scheme can be expressed as

$$1/k_{eff} = (k_b/k_a k_c)(1/P_{O2}) + (1/k_a)(1/P_M)$$

where P_{O2} is the partial pressure of O_2 and P_M equals $P_{O2} + P_{N2}$. The validity of this expression requires that k_a and k_b are invariant with the P_{O2}/P_{N2} ratio. A $1/k$ vs $1/P_{O2}$ plot of the data of Jones et al (taken at atmospheric pressure) exhibits marked curvature, suggesting a more complex mechanistic involvement of O_2, whereas the data of Barnes et al and Hynes et al are more satisfactorily represented by this analysis. Nevertheless, while the qualitative features of the data from all three laboratories agree, there are some quantitative inconsistencies. First, under similar conditions of O_2 and N_2 pressures, the Barnes et al rate constants lie approximately 60% higher than those of Jones et al and up to a factor of 2 higher than the measurements by Ravishankara et al. Secondly, two fits each of both the Barnes and Hynes data can be made: one at fixed P_M and varying P_{O2}, and the other at fixed P_{O2} and varying P_M (i.e., varying added N_2). Within each data set, rate constants calculated from both fits agree reasonably well for mole fractions of O_2 near 0.2 (equivalent to air), but disagree by more than a factor of 2 for measurements in a pure O_2 system. Finally, the temperature dependence (from 264-293 K) of the k_{eff} values from Barnes et al varies systematically from an E/R of -1300 K for runs in pure O_2 (at 700 torr total pressure) to -2900 K in a 50 torr O_2 plus 650 torr N_2 mixture. An Arrhenius fit of the Hynes et al data (from 251-348 K) recorded in synthetic air at 690 torr yields an E/R = -3300 K, although the data show marked curvature over the temperature range of study. These observations suggest that k_a and k_b may not be independent of the identity of M. For this reason, we limit our recommendation to air mixtures (i.e., $P_{O2}/P_{N2} = 0.25$) at atmospheric pressure. Since most CS_2 is oxidized within the atmospheric boundary layer, such restriction does not limit the applicability of this recommendation in atmospheric modeling.

The present recommendation accepts the measurements of Hynes et al (1988) which appear to be the most sensitive of the three investigations. Thus, k(298 K) is derived from the Arrhenius fit of the data near room temperature

$$k(298 \text{ K}) = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The uncertainty factor ($f_{298} = 1.5$) encompasses the results of Barnes et al (1983) within 2σ. To compute values of k below 298 K we have accepted the analysis by Hynes et al.

$$k(T) = \{1.25 \times 10^{-16} \exp(4550/T)\}/\{T + 1.81 \times 10^{-3} \exp(3400/T)\}$$

Again, this recommendation is valid only for one atmosphere pressure of air. It is interesting to note that measurements by Hynes et al (1988) at approximately 250 K and 700 torr total pressure result in k_{eff} values which are independent of the amount of O_2 for partial pressures between 145-680 torr. This suggests that the adduct is quite stable with respect to dissociation into the reactants (OH + CS_2) at this low temperature and the effective rate constant for reactant removal approaches the elementary rate constant for the adduct formation. Clearly additional work may be needed before the full details of this complex reaction are understood.

H4.   O + H_2S. This recommendation is derived from an unweighted least squares fit of the data of Singleton et al (1979) and Whytock et al (1976). The results of Slagle et al (1978) show very good agreement for E/R in the temperature region of overlap (300-500 K) but lie systematically higher at every temperature. The uncertainty factor at 298 K has been chosen to encompass the values of k(298 K) determined by Slagle et al (1978) and Hollinden et al (1970). Other than the 263 K data point of Whytock et al (1976) and the 281 K point of Slagle et al (1978) the main body of rate constant data below 298 K comes from the study of Hollinden et al (1970), which indicates a dramatic change in E/R in this temperature region. Thus, ΔE/R was set to account for these observations. Such a non-linearity in the Arrhenius plot might indicate a change in the reaction mechanism from abstraction (as written) to addition. An additional channel (resulting in H-atom displacement) has been proposed for this reaction by Slagle et al (1978), Singleton et al (1979), and Singleton et al (1982). In the two Singleton studies an upper limit of 20% is placed

on the displacement channel. Direct observation of product HSO was made in the recent reactive scattering experiments of Clemo et al (1981) and Davidson et al (1982). A threshold energy of 3.3 kcal/mole was observed (similar to the activation energy measured in earlier studies) suggesting the importance of this direct displacement channel. Addition products from this reaction have been seen in a matrix by Smardzewski and Lin (1977). Further kinetics studies in the 200 to 300 K range as well as quantitative direct mechanistic information could clarify these issues. This reaction is thought to be of limited stratospheric importance, however.

H5.   O + OCS. The value for k(298 K) is the average of five different studies of this reaction: Westenberg and de Haas (1969a), Klemm and Stief (1974), Wei and Timmons (1975), Manning et al (1976) and Breckenridge and Miller (1972). The recommended value for E/R is the average of those determined in the temperature studies reported in the first three references. Hsu et al (1979) report that this reaction proceeds exclusively by a stripping mechanism.

H6.   O + CS_2. The value of k(298 K) is the average of seven determinations: Wei and Timmons (1975), Westenberg and de Haas (1969a), Slagle et al (1974a), Callear and Smith (1967), Callear and Hedges (1970), Homann et al (1968), and Graham and Gutman (1977). The E/R value is an average of those determined by Wei and Timmons (1975) and Graham and Gutman (1977). ΔE/R has been set to encompass the limited temperature data of Westenberg and de Haas (1969a). The principal reaction products are thought to be CS + SO. However, Hsu et al (1979) report that 1.4% of the reaction at 298 K proceeds through the channel yielding CO + S_2 and calculate a rate constant for the overall process in agreement with that recommended. Graham and Gutman (1977) have found that 9.6% of the reaction proceeds to yield OCS + S at room temperature.

H7.   S + O_2. This recommendation is based primarily on the study of Davis et al (1972). Modest agreement at 298 K is provided by the studies of Fair and Thrush (1969), Fair et al (1971), Donovan and Little (1972) and Clyne and Townsend (1975). The study by Clyne and Whitefield (1979), which indicates a slightly negative E/R between 300 and 400 K, is encompassed by the present recommendation.

H8.   S + O_3. This recommendation accepts the only available experimental data; that from Clyne and Townsend (1975). In the same study these authors report a value for S + O_2 in reasonable agreement with that recommended. The error limit cited reflects both the agreement and the need for independent confirmation.

H9.   S + OH. This recommendation is based on the single study by Jourdain et al (1979). Their measured value for k(298 K) compares favorably with the recommended value of k(O + OH) when one considers the slightly greater exothermicity of the present reaction.

H10.   SO + O_2. This recommendation is based on the low temperature measurements of Black et al (1982a, 1982b). The room temperature value accepts the latter results, as recommended by the authors. The uncertainties cited reflect the need for further confirmation and the fact that these results lie significantly higher than an extrapolation of the higher temperature data of Homann et al (1968). A room temperature upper limit on k set by Breckenridge and Miller (1972) is in good agreement with the Black et al data.

H11.   SO + O_3. The value of k(298 K) is an average of the determinations by Halstead and Thrush (1966), Robertshaw and Smith (1980), and Black et al (1982a, 1982b) using widely differing techniques. The value of E/R is an average of the values reported by Halstead and Thrush (1966) and Black et al (1982b), with the A-factor calculated to fit the value recommended for k(298 K).

H12.   SO + OH. The value recommended for k(298 K) is an average of the determinations by Fair and Thrush (1969) and Jourdain et al (1979). Both sets of data have been corrected using the present recommendation for the O + OH reaction.

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H13. SO + NO$_2$. The value of k(298 K) is an average of the measurements by Clyne and MacRobert (1980), Black et al (1982a), and Brunning and Stief (1986a), which agree quite well with the rate constant calculated from the relative rate measurements of Clyne et al (1966). The Arrhenius parameters are taken from Brunning and Stief (1986a).

H14. SO + ClO. The value of k(298 K) is an average of the measurements by Clyne and MacRobert (1981) and by Brunning and Stief (1986a). The temperature independence is taken from Brunning and Stief, with the A-factor calculated to fit the value of k(298 K).

H15. SO + OClO. This recommendation is based on the single room temperature study by Clyne and MacRobert (1981). The uncertainty reflects the absence of any confirming investigation.

H16. SO + BrO. This recommendation is based on the measurements of Brunning and Stief (1986b) performed under both excess BrO and excess SO conditions. The rate constant is supported by the lower limit assigned by Clyne and MacRobert (1981) from measurements of SO$_2$ production.

H17. SO$_2$ + HO$_2$. This upper limit is based on the atmospheric pressure study of Graham et al (1979). A low pressure laser magnetic resonance study by Burrows et al (1979) places a somewhat higher upper limit on k(298 K) of 4×10^{-17} (determined relative to OH + H$_2$O$_2$). Their limit is based on the assumption that the products are OH + SO$_3$. The weight of both these studies suggests an error in the earlier determination by Payne et al (1973).

H18. SO$_2$ + CH$_3$O$_2$. This recommendation accepts results from the study of Sander and Watson (1981a), which is believed to be the most appropriate study for stratospheric modeling purposes among those which have been conducted. Their experiments were conducted using much lower CH$_3$O$_2$ radical concentrations than in the earlier studies of Sanhueza et al (1979) and Kan et al (1979), both of which resulted in k(298 K) values approximately 100 times larger. A later report by Kan et al (1981) postulates that these differences are due to the reactive removal of the CH$_3$O$_2$SO$_2$ adduct at high CH$_3$O$_2$ radical concentrations, prior to its reversible decomposition into CH$_3$O$_2$ + SO$_2$. They suggest that such behavior of CH$_2$O$_2$SO$_2$ or its equilibrated adduct with O$_2$ (CH$_3$O$_2$SO$_2$O$_2$) would be expected in the studies yielding high k values, while decomposition of CH$_3$O$_2$SO$_2$ into reactants would dominate in the Sander and Watson experiments. It does not appear likely that such secondary reactions involving CH$_3$O$_2$, NO, or other radical species, if they occur, would be rapid enough under normal stratosphere conditions to complete with the adduct decomposition. This interpretation, unfortunately, does not explain the high rate constant derived by Cocks et al (1986) under conditions of low [CH$_3$O$_2$].

H19. SO$_2$ + NO$_2$; SO$_3$ + NO$_2$. The recommendations for both of these reactions are based on the study of Penzhorn and Canosa (1983) using second derivative uv spectroscopy. The upper limit given for k(298 K) in the SO$_2$ reaction is actually their measured value. However, their observations of strong heterogeneous and water vapor catalyzed effects prompt us to accept their measurement as an upper limit. This value is approximately two orders of magnitude lower than that for a dark reaction observed by Jaffe and Klein (1966) in NO$_2$ + SO$_2$ mixtures (much of which may have been due to heterogeneous processes). Penzhorn and Canosa suggest the products of the SO$_2$ reaction to be NO + SO$_3$. They observe a white aerosol produced in the reaction of NO$_2$ with SO$_3$ and interpret it to be the adduct NSO$_5$. This claim is supported by ESCA spectra.

H20. SO$_2$ + NO$_3$. This recommended upper limit on k(298 K) is the result of Daubendiek and Calvert (1975). Considerably more conservative upper limits have been derived by Burrows et al (1985b) and Wallington et al (1986a), Canosa-Mas et al (1988), and Dlugokencky and Howard (1988).

H21. SO$_2$ + O$_3$. This recommendation is based on the limited data of Davis et al (1974b) at 300 K and 360 K in a stopped-flow investigation using mass spectrometric and uv spectroscopic detection.

H22. SO_3 + H_2O. New Entry. This recommendation is based on the measurements of Wang et al (1988). Although these authors attempted to exclude any heterogeneous effects from their experiments, they conclude that their measurements must still be viewed as yielding an upper limit to the gas phase homogeneous reaction rate. An earlier reported higher rate constant value by Castleman et al (1975) may have resulted from an underestimation of the effects of heterogeneous reaction in this study.

H23. Cl + H_2S. The value of k(298 K) is an average of the measurements by Nesbitt and Leone (1980), which refines the data of Braithwaite and Leone (1978), Clyne and Ono (1983), Clyne et al (1984), and Nava et al (1985). The zero activation energy is derived from the data of Nava et al and the A-factor is calculated to agree with k(298 K). Lu et al (1986) also measure a temperature independent rate constant, and their larger value of k(298 K) = 10.5 x 10^{-11} may be indicative of a slight pressure dependence for the reaction, since their experiments were performed at 4000 torr.

H24. Cl + OCS. This upper limit is based on the minimum detectable decrease in atomic chlorine measured by Eibling and Kaufman (1983). Based on the observation of product SCl, these authors set a lower limit on k(298 K) of 10^{-18} for the reaction as written. Considerably more conservative upper limits on k(298 K) were determined in the studies of Clyne et al (1984) and Nava et al (1985).

H25. ClO + OCS; ClO + SO_2. These recommendations are based on the discharge flow mass spectrometric data of Eibling and Kaufman (1983). The upper limit on k(298 K) for ClO + OCS was set from the minimum detectable decrease of ClO in this reaction system. No products were observed. The upper limit on k(298 K) for ClO + SO_2 is based on the authors' estimate of their detectability for SO_3. Their estimates of k(298 K) based on the minimum detectable decrease in ClO have not been used because of the potential problem of ClO reformation from the Cl + O_3 source reaction.

H26. SH + H_2O_2. This recommended upper limit for k(298 K) is based on the single study of Friedl et al (1985). Their value is calculated from the lack of SH decay (measured by laser-induced fluorescence) and the lack of OH production (measured by resonance fluorescence). The three possible product channels are: H_2S + HO_2, HSOH + OH, and HSO + H_2O.

H27. SH + O. This recommendation accepts the results of Cupitt and Glass (1975). The large uncertainty reflects the fact that there is only one study of the reaction.

H28. SH + O_2. This upper limit for k(298 K) is based on the study by Stachnik and Molina (1987) in experiments sensitive to the production of OH. More conservative upper limits on k(298 K) of 1.0 x 10^{-17} and 1.5 x 10^{-17} were assigned by Friedl et al (1985) and Wang et al (1987) respectively from detection sensitivities for OH production and SH decay, respectively. An even higher upper limit by Black (1984), based on the lack of SH decay, may have been complicated by SH regeneration. Much less sensitive upper limits had been calculated by Tiee et al (1981), Nielsen (1979), and Cupitt and Glass (1975). Stachnik and Molina (1987) also report a more conservative upper limit (<1.0 x 10^{-18}) for the rate constant for the sum of the two SH + O_2 reaction channels (producing OH + SO and H + SO_2).

H29. SH + O_3. The value for k(298 K) is an average of the determinations by Friedl et al (1985) (laser induced fluorescence detection of SH), Schonle et al (1987) (mass spectrometric detection of reactant SH and product HSO) as revised by Schindler and Benter (1988), and Wang and Howard (1989) (laser magnetic resonance detection of SH). The temperature dependence is from Wang and Howard, with the A-factor calculated to agree with the recommended value of k(298 K). Δ(E/R) reflects the fact that the temperature dependence comes from measurements above room temperature and thus extrapolation to lower temperatures may have additional uncertainties.

H30. SH + NO_2. This recommendation accepts the measurements by Wang et al (1987). These authors suggest that the lower values of k(298 K) measured by Black (1984), Friedl et al (1985), and Bulatov et al

(1985) are due to SH regeneration from the H_2S source compound. In the recent study by Stachnik and Molina (1987), attempts were made at minimizing such regeneration. These authors obtained a k(298 K) value significantly higher than did the earlier investigators, but still 30% lower than that measured by Wang et al, who used two independent SH source reactions. A slightly higher rate constant value measured by Schonle et al (1987) as revised by Schindler and Benter (1988) has not been recommended due to the somewhat limited data base for their determination. The reaction as written represents the most exothermic channel. The absence of a primary isotope effect, as observed by Wang et al (1987), coupled with the large magnitude of the rate constant, suggests that the (four-center intermediate) channels producing SO + HNO and OH + SNO are of minor importance. No evidence for a three-body combination reaction was found by either Black (1984) or Friedl et al (1985). Based on a pressure independence of the rate constant between 30 and 300 torr, Black set an upper limit of 7.0×10^{-31} for the third body rate constant. Similarly, Stachnik and Molina (1987) saw no change in decay rate between 100 and 730 torr with O_2 (although these O_2 experiments were designed primarily to limit SH regeneration).

H31. HSO + NO, HSO + NO_2, HSO + O_2. These recommendations for all three reactions are based on the measurements of Lovejoy et al (1987), who used laser magnetic resonance detection to monitor HSO in a discharge flow reactor. Their upper limit for the NO reaction is a factor of 25 lower than the rate constant measured by Bulatov et al (1985) using intracavity laser absorption at pressures between 10 and 100 torr. Since it is unlikely that this reaction rate undergoes a factor of 25 increase between 1 torr (the pressure of the Lovejoy et al work) and 10 torr, the higher rate constant may be due to secondary chemistry associated with the HSO production.

The recommendation for the NO_2 reaction is a factor of two higher than the rate constant reported by Bulatov et al (1984). Lovejoy et al have attributed this difference to HSO regeneration under the experimental conditions used by Bulatov et al. (1984). The product assignment for the NO_2 reaction is discussed in note H33.·

H32. HSO + O_3. This recommendation is based on the single determination by Friedl et al (1985) in their study of the SH + O_3 reaction. At higher O_3 concentrations, greater quantities of HSO were produced in the flow tube and SH approached a steady state due to its regeneration via HSO + O_3. The rate constant for this latter reaction was thus determined relative to SH + O_3 from measurements of the steady state SH concentration as a function of the initial SH concentration. The lack of an isotope effect when SD was employed suggests that the products of the HSO + O_3 reaction are SH + $2O_2$ (analogous to those for $HO_2 + O_3$).

H33. HSO_2 + O_2. This recommendation is based on the rate of HO_2 formation measured by Lovejoy et al (1987) upon addition of O_2 to the HSO + NO_2 reaction system. While HSO_2 was not observed directly, a consideration of the mechanistic possibilities for HSO + NO_2, coupled with measurements of the HO_2 production rate at various O_2 pressures, led these authors to suggest that HSO_2 is both a major product of the HSO + NO_2 reaction and a precursor for HO_2 via reaction with O_2.

H34. $HOSO_2$ + O_2. This recommendation is based on the studies of Gleason et al (1987) and Gleason and Howard (1988), in which the $HOSO_2$ reactant was directly monitored using a chemical ionization mass spectrometric technique. Gleason and Howard conducted their measurements over the 297-423 K temperature range, constituting the only temperature dependence investigation. Thus $\Delta E/R$ has been increased from their quoted limits to account for the potential uncertainties in extrapolating their data to subambient temperatures. The value of k(298 K) derives further support from the studies of Margitan (1984a) and Martin et al (1986), both of whom used modeling fits of OH radical decays in the OH + SO_2 + M reaction system in the presence of O_2 and NO. In this latter analysis, the $HOSO_2$ (produced by OH + SO_2 + M) reacts with O_2 yielding HO_2, which subsequently regenerates OH through its reaction with NO. The infrared spectrum of $HOSO_2$ has been recorded in low tempera-

ture matrix isolation experiments by Hashimoto et al (1984) and Nagase et al (1988). Mass spectrometric detection of HOSO$_2$ in the gas phase has also been reported by Egsgaard et al (1988).

H35. H$_2$S + NO$_3$. This recommendation accepts the upper limit set by Dlugokencky and Howard (1988) based on experiments in which the NO$_3$ loss was followed in the presence of large concentrations of H$_2$S. More conservative upper limits for the rate constant have been reported by Wallington et al (1986a) and Cantrell et al (1987).

H36. CS + O$_2$. The recommendation given for k(298 K) is based on the work of Black et al (1983) using LIF to monitor CS decays. This value agrees with the somewhat less precise determination by Richardson (1975) using OCS formation rates, suggesting the validity of the reaction products as written. The latter author presents evidence that this reaction channel dominates the one producing SO + CO by more than a factor of 10. Measurements by Richardson at 293 K and 495 K yield an E/R value of 1860 K. However, use of this activation energy with the recommended value of k(298 K) results in an unusually low Arrhenius A-factor of 1.5 x 10^{-16}. In view of this, no recommendation is presently given for the temperature dependence.

H37. CS + O$_3$; CS + NO$_2$. The k(298 K) recommendations for both reactions accept the results of Black et al (1983), who used LIF real-time detection of CS in a laser photolysis experiment at room temperature. The uncertainty factor reflects the absence of any confirming measurements.

H38. OH + CH$_3$SH. New Entry. The recommended values were derived from a composite fit to the data of Atkinson et al (1977b), Wine et al (1981a), Wine et al (1984a), and Hynes and Wine (1987) which are all in excellent agreement. The results from the relative rate study of Barnes et al (1986) are in agreement with this recommendation and indicate that the higher values of Cox and Sheppard (1980) are due to complications resulting from the presence of O$_2$ and NO in their reaction system. MacLeod et al (1983, 1984) and Lee and Tang (1983) obtained rate constants at 298 K approximately 50% lower than recommended here. These authors also obtained lower values for the ethanethiol reaction when compared with the studies upon which the methanethiol recommendation is made. Wine et al (1984a) present evidence that this reaction proceeds via adduct formation to produce a species which is thermally stable over the temperature range and time scales of the kinetic measurements. Hynes and Wine (1987) failed to observe any effect of O$_2$ on the measured rate constant.

H39. OH + CH$_3$SCH$_3$. New Entry. This recommendation averages the results of Hynes et al (1986b), and Wine et al (1981a) with those of Hsu et al (1987c). The earlier, higher rate constant values of Atkinson et al (1978) and Kurylo (1978a) were presumably due to reactive impurities, while those of MacLeod et al (1983) were most likely overestimated because of heterogeneous reactions. Rate constants lower than those recommended were obtained by Martin et al (1985), Wallington et al (1986b), and Nielsen et al (1989). While the reasons for these differences are not readily apparent, these results are encompassed within the 2σ error limit of the recommendation. Hynes et al (1986b) have demonstrated the importance of a second reaction channel involving addition of OH to dimethyl sulfide. The adduct formed decomposed rapidly, so that in the absence of any adduct scavenger only the direct abstraction channel is measured. The recommendation given in Table 1 is for the abstraction reaction. In the presence of O$_2$, however, the adduct reacts to form a variety of products. This effect of O$_2$ has been suggested as an explanation for the higher rate constants obtained in many of the earlier relative rate studies. Hynes et al (1986b) give the following expression:

$$k_{obs} = \{T \exp(-234/T) + 8.46 \times 10^{-10} \exp(7230/T) + 2.68 \times 10^{-10} \exp(7810/T)\}/$$

$$\{1.04 \times 10^{11} T + 88.1 \exp(7460/T)\}$$

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H40. OH + CH$_3$SSCH$_3$. New Entry. This recommendation is based on the study of Wine et al (1981a). The room Temperature relative rate study by Cox and Sheppard (1980) is in good agreement with the recommended value. The value of $\Delta E/R$ reflects the existence of only one temperature dependence investigation.

H41. NO$_3$ + CH$_3$SH. New Entry. The recommended values are derived from a composite fit to the data of Wallington et al (1986a), Rahman et al (1988), and Dlugokencky and Howard (1988). The room temperature rate constant derived in the relative rate experiments of MacLeod et al (1986) is in good agreement with the recommended value. The experimental data from these investigations show that the rate constant is independent of pressure over the range 1-700 torr.

H42. NO$_3$ + CH$_3$SCH$_3$. New Entry. The recommended values are derived from a composite fit to the data of Wallington et al (1986a), Tyndall et al (1986), and Dlugokencky and Howard (1988). The relative rate study of Atkinson et al (1984b) gives a room temperature rate constant in good agreement with this recommendation. The experimental data from these investigations show that the rate constant is independent of pressure over the range 1-740 torr. A recent room temperature study by Daykin and Wine (1989) is also in agreement with the recommended value.

H43. NO$_3$ + CH$_3$SSCH$_3$. New Entry. The recommended values were derived from a composite fit to the data of Wallington et al (1986a) and Dlugokencky and Howard (1988). A recent relative rate investigation by Atkinson et al (1988) indicates that the relative rate technique cannot be considered as yielding reliable rate data for this reaction due to chemical complexities. Thus, the much lower room temperature results from the study of MacLeod et al (1986) can be considered to be in error.

H44. NO$_3$ + CS$_2$. New Entry. This upper limit is based on the study of Burrows et al (1985b). A more conservative upper limit was derived in the relative rate study of MacLeod et al (1986.

H45. NO$_3$ + OCS. New Entry. This upper limit is based on the relative rate data of MacLeod et al (1986).

H46. CH$_3$S + O$_2$. New Entry. This upper limit is based on the recent study of Tyndall and Ravishankara (1989a). More conservative upper limits were derived in earlier studies by Balla et al (1986) and Black and Jusinski (1986).

H47. CH$_3$S + O$_3$. New Entry. This recommendation is based on the single room temperature determination of Tyndall and Ravishankara (1989b). A failure to observe significant reaction in the earlier study of Black and Jusinski (1986) is interpreted as due to rapid regeneration of CH$_3$S in their system. The uncertainty factor reflects the analysis difficulties and the absence of additional confirming studies.

H48. CH$_3$S + NO$_2$. New Entry. This recommendation averages the recent results of Tyndall and Ravishankara (1989a) and Domine and Howard (1989). An earlier study by Balla et al (1986) yielded a room temperature rate constant nearly a factor of 2 higher which may be attributed to secondary reactions at higher radical concentrations.

H49. CH$_3$SO + O$_3$. New Entry. This recommendation is based on the study of Tyndall and Ravishankara (1989b). These authors derive this value from a complex analysis of the CH$_3$S + O$_3$ reaction system.

H50. CH$_3$SO + NO$_2$. New Entry. This recommendation is based on the direct measurements of Domine and Howard (1989). The results are supported by the somewhat less direct measurements of Tyndall and Ravishankara (1989a) who modeled NO formation in the CH$_3$S + NO$_2$ reaction system.

J1. $Na + O_3$. The recommendation is the average of measurements of Worsnop et al (1989) and Ager et al (1986). These values are in excellent agreement. The data of Worsnop et al supersedes earlier work from that laboratory (Silver and Kolb, 1986a). Measurements made by Husain et al (1985) at 500 K are consistent with the recommendation but are not included because they did not recognize that secondary chemistry, $NaO + O_3 \rightarrow Na + 2O_2$, interferes with the rate coefficient measurement. Ager et al (1986) estimate that the $NaO_2 + O$ product channel $\leq 5\%$.

J2. $Na + N_2O$. The recommendation incorporates the data of Husain and Marshall (1985), Ager et al (1986), and Silver and Kolb (1986a). Husain and Marshall and Ager et al measured the temperature dependence over the ranges 349 to 917 K and 240 to 429 K, respectively, and are in good agreement. Measurements by Plane and Rajasekhar (1988) and Worsnop et al (1989) are consistent with the recommendation. Silver and Kolb measured a rate coefficient at 295 K which is about 35% lower than the other two. Earlier less direct studies are discussed by Ager et al (1986). The NaO product does not react significantly with N_2O at room temperature (k (for $Na + N_2 + O_2$ products) $\leq 10^{-16}$ cm^3 molecule^{-1} s^{-1} and k (for $NaO_2 + N_2$) $\leq 2 \times 10^{-15}$ Ager et al).

J3. $Na + Cl_2$. Two measurements of the rate coefficient for this reaction are in excellent agreement: Silver (1986) and Talcott et al (1986). The recommended value is the average of these room temperature results.

J4. $NaO + O$. The recommendation is based on a measurement at 573 K by Plane and Husain (1986). They reported that $\leq 1\%$ of the Na product is in the 3^2P excited state.

J5. $NaO + O_3$. This reaction was studied by Silver and Kolb (1986a) and Ager et al (1986), who agree on the rate coefficient and branching ratio. This agreement may be fortuitous because Silver and Kolb used an indirect method and an analysis based on their rate coefficient for the $Na + O_3$ reaction which is about 1/2 that reported by Ager et al. Ager et al employed a somewhat more direct measurement but the study is complicated by a chain reaction mechanism in the Na/O_3 system.

J6. $NaO + H_2$. The recommendation is based on a measurement by Ager and Howard (1987a). They also reported a significant $Na + H_2O$ product channel and that a small fraction of the Na from this channel is in the 3^2P excited state.

J7. $NaO + H_2O$. The recommendation is based on a measurement by Ager and Howard (1987a).

J8. $NaO + NO$. The recommendation is based on an indirect measurement reported by Ager et al (1986).

J9. $NaO + HCl$. There is only one indirect measurement of the rate coefficient for this reaction, that from the study of Silver et al (1984a). They indicate that the products are NaCl and OH, although some NaOH and Cl production is not ruled out.

J10. $NaO_2 + NO$. This reaction is endothermic. The upper limit recommended is from an experimental study by Ager et al (1986).

J11. $NaO_2 + HCl$. The recommendation is based on a measurement reported by Silver and Kolb (1986b). They indicated that the products are $NaCl + HO_2$, but $NaOOH + Cl$ may be possible products.

J12. $NaOH + HCl$. The recommendation is based on the study of Silver et al (1984a), which is the only published study of this reaction.

Table 2. Rate Constants for Three-Body Reactions

Reaction	Low Pressure Limit[a] $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		Notes
	k_o^{300}	n	k_∞^{300}	m	
& $O + O_2 \xrightarrow{M} O_3$	(6.0±0.5)(-34)	2.3±0.5	-	-	1
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(3.5±3.0)(-37)	$0.6^{+2.0}_{-0.6}$	-	-	2
& $H + O_2 \xrightarrow{M} HO_2$	(5.7±0.5)(-32)	1.6±0.5	(7.5±4.0)(-11)	0±1	3
* $OH + OH \xrightarrow{M} H_2O_2$	(6.9±3.0)(-31)	$0.8^{+2.0}_{-0.8}$	(1.5±0.5)(-11)	0±0.5	4
$O + NO \xrightarrow{M} NO_2$	(9.0±2.0)(-32)	1.5±0.3	(3.0±1.0)(-11)	0±1	5
$O + NO_2 \xrightarrow{M} NO_3$	(9.0±1.0)(-32)	2.0±1.0	(2.2±0.3)(-11)	0±1	6
$OH + NO \xrightarrow{M} HONO$	(7.0±2.0)(-31)	2.6±1.0	(1.5±1.0)(-11)	0.5±0.5	7
$OH + NO_2 \xrightarrow{M} HNO_3$	(2.6±0.3)(-30)	3.2±0.7	(2.4±1.2)(-11)	1.3±1.3	8
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(1.8±0.3)(-31)	3.2±0.4	(4.7±1.0)(-12)	1.4±1.4	9
& $NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(2.2±0.5)(-30)	4.3±1.3	(1.5±0.8)(-12)	0.5±0.5	10
$Cl + NO \xrightarrow{M} ClNO$	(9.0±2.0)(-32)	1.6±0.5	-	-	11
$Cl + NO_2 \xrightarrow{M} ClONO$	(1.3±0.2)(-30)	2.0±1.0	(1.0±0.5)(-10)	1±1	12
$\xrightarrow{M} ClNO_2$	(1.8±0.3)(-31)	2.0±1.0	(1.0±0.5)(-10)	1±1	12
* $Cl + O_2 \xrightarrow{M} ClOO$	(2.7±1.0)(-33)	1.5±0.5	-	-	13
# $Cl + CO \xrightarrow{M} ClCO$	(1.3±0.5)(-33)	3.8±0.5	-	-	14
* $Cl + C_2H_2 \xrightarrow{M} ClC_2H_2$	(8.0±1.0)(-30)	3.5±0.5	(1.0±0.5)(-10)	2.6±0.5	15
* $ClO + ClO \xrightarrow{M} Cl_2O_2$	(1.8±0.5)(-32)	3.6±1.0	(6.0±2)(-12)	0±1	16
& $ClO + NO_2 \xrightarrow{M} ClONO_2$	(1.8±0.3)(-31)	3.4±1.0	(1.5±0.7)(-11)	1.9±1.9	17

Note: $k(Z) = k(M,T) = \left(\dfrac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)}\right) 0.6^{\{1 + [\log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}$

The values quoted are suitable for air as the third body, M.

a Units are $cm^6/molecule^2$-sec

b Units are $cm^3/molecule$-sec

* Indicates a change from the previous Panel evaluation (JPL 87-41).

& Indicates a change in the note from the previous evaluation.

# Indicates a new entry that was not in the previous evaluation.

Table 2. (Continued)

Reaction	Low Pressure Limit[a] $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		Notes
	k_o^{300}	n	k_∞^{300}	m	
* $BrO + NO_2 \xrightarrow{M} BrONO_2$	(5.2±0.5)(-31)	3.8±1.0	(9.0±1.0)(-12)	2.3±1.0	18
* $F + O_2 \xrightarrow{M} FO_2$	(4.4±0.4)(-33)	1.2±0.5	-	-	19
$F + NO \xrightarrow{M} FNO$	(5.9±3.0)(-32)	1.7±1.7	-	-	20
$F + NO_2 \xrightarrow{M} Products$	(1.1±0.6)(-30)	2.0±2.0	(3.0±2.0)(-11)	1±1	21
$FO + NO_2 \xrightarrow{M} FONO_2$	(2.6±2.0)(-31)	1.3±1.3	(2.0±1.0)(-11)	1.5±1.5	22
* $CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(4.5±1.5)(-31)	3.0±1.0	(1.8±0.2)(-12)	1.7±1.7	23
# $C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2$	(2.0±1.5)(-28)	3.8±1.0	(5.0±3.0)(-12)	0±1	24
& $CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(1.5±0.8)(-30)	4.0±2.0	(6.5±3.2)(-12)	2±2	25
$OH + SO_2 \xrightarrow{M} HOSO_2$	(3.0±1.0)(-31)	3.3±1.5	(1.5±0.5)(-12)	0^{+0}_{-2}	26
$OH + C_2H_4 \xrightarrow{M} HOCH_2CH_2$	(1.5±0.6)(-28)	0.8±2.0	(8.8±0.9)(-12)	0^{+0}_{-2}	27
& $OH + C_2H_2 \xrightarrow{M} HOCHCH$	(5.5±2.0)(-30)	0.0±0.2	(8.3±1.0)(-13)	-2^{+2}_{-1}	28
$CF_3 + O_2 \xrightarrow{M} CF_3O_2$	(1.5±0.3)(-29)	4±2	(8.5±1.0)(-12)	1±1	29
$CFCl_2 + O_2 \xrightarrow{M} CFCl_2O_2$	(5.0±0.8)(-30)	2±2	(6.0±1.0)(-12)	1±1	30
$CCl_3 + O_2 \xrightarrow{M} CCl_3O_2$	(1.0±0.7)(-30)	2±2	(2.5±2)(-12)	1±1	31
* $CFCl_2O_2 + NO_2 \xrightarrow{M} CFCl_2O_2NO_2$	(3.5±0.5)(-29)	5±1	(6.0±1.0)(-12)	2.5±1	32
# $CF_3O_2 + NO_2 \xrightarrow{M} CF_3O_2NO_2$	(2.2±0.5)(-29)	5±1	(6.0±1.0)(-12)	2.5±1	33
# $CCl_3O_2 + NO_2 \xrightarrow{M} CCl_3O_2NO_2$	(5.0±1.0)(-29)	5±1	(6.0±1.0)(-12)	2.5±1	34
$HS + NO \xrightarrow{M} HSNO$	(2.4±0.4)(-31)	3±1	(2.7±0.5)(-11)	0^{+0}_{-2}	35

Note: $k(Z) = k(M,T) = (\dfrac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)}) 0.6^{\{1 + [\log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}$

The values quoted are suitable for air as the third body, M.

a Units are $cm^6/molecule^2$-sec

b Units are $cm^3/molecule$-sec

* Indicates a change from the previous Panel evaluation (JPL 87-41).

& Indicates a change in the note from the previous evaluation.

# Indicates a new entry that was not in the previous evaluation.

Table 2. (Continued)

Reaction	Low Pressure Limit[a] $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		Notes
	k_o^{300}	n	k_∞^{300}	m	
* Na + O$_2$ $\xrightarrow{M}$ NaO$_2$	(2.4±0.5)(-30)	1.2±0.5	(4.0±2.0)(-10)	0±1	36
NaO + O$_2$ $\xrightarrow{M}$ NaO$_3$	(3.5±0.7)(-30)	2±2	(5.7±3)(-10)	0±1	37
NaO + CO$_2$ $\xrightarrow{M}$ NaCO$_3$	(8.7±2.6)(-28)	2±2	(6.5±3)(-10)	0±1	38
NaOH + CO$_2$ $\xrightarrow{M}$ NaHCO$_3$	(1.3±0.3)(-28)	2±2	(6.8±4)(-10)	0±1	39

Note: $k(Z) = k(M,T) = \left(\dfrac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)}\right) 0.6^{\{1 + [\log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}$

The values quoted are suitable for air as the third body, M.

a Units are cm^6/molecule^2-sec

b Units are cm^3/molecule-sec

* Indicates a change from the previous Panel evaluation (JPL 87-41).

& Indicates a change in the note from the previous evaluation.

# Indicates a new entry that was not in the previous evaluation.

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NOTES TO TABLE 2

1. $O + O_2$. Low-pressure limit and T-dependence are an average of Klais, Anderson, and Kurylo (1980a), and Lin and Leu (1982). The result is in agreement with most previous work (see references therein). Kaye (1986) has calculated isotope effects for this reaction, using methods similar to those discussed in the Introduction; Troe (1977), Patrick and Golden (1983). Croce de Cobos and Troe (1984) are in agreement with earlier work. Rawlins et al (1987) report values in Ar between 80 and 150 K that extrapolate to agreement with the recommended values.

2. $O(^1D) + N_2$. Low-pressure limit from Kajimoto and Cvetanovic (1976). The T-dependence is obtained by assuming a constant β. The rate constant is extremely low in this special system due to electronic curve crossing.

3. $H + O_2$. Kurylo (1972), Wong and Davis (1974) and Hsu et al (1987) are averaged to obtain the low pressure limiting value at 300 K. The first two studies include T-dependence, as does a recent study by Hsu et al (1989). The recommended value is chosen with constant $<\Delta E>_{N_2} \sim .05$ kcal mole^{-1}. This very low number reflects rotational effects. The high pressure limit is from Cobos et al (1985). The temperature dependence is estimated. Cobos et al (1985) estimate m = -0.6, which is within our uncertainty. Recent high temperature measurements in Ar by Pirraglia et al (1989) are in good agreement.

4. $OH + OH$. Zellner et al (1988) have studied this reaction at 253, 298, and 353 K at pressures between 26 and 1100 mbar of N_2. They report

$$k_o(T) = 6.9^{+1.4}_{-2.5}) \times 10^{-31} (T/298)^{-0.8} \text{ cm}^3 \text{ s}^{-1}$$

$$k_\infty(T) = 1.5 \times 10^{-11} (T/298)^0 \text{ cm}^3 \text{ s}^{-1}$$

The asymmetric error limits in k_o (298) take into account contributions from $H + OH \rightarrow H_2O$. Error limits were not reported for other parameters. The recommended error limits are estimates. Trainor and von Rosenberg (1974) report a value at 300 K that is lower by a factor of 2.7.

5. $O + NO$. Low-pressure limit and n from direct measurements of Schieferstein et al (1983) and their re-analysis of the data of Whytock et al (1976). Error limits encompass other studies. High-pressure limit and m from Baulch et al (1980) and Baulch et al (1982), slightly modified.

6. $O + NO_2$. Values of rate constants and temperature dependences from the evaluations of Baulch et al (1980). They use $F_c = 0.8$ to fit the measured data at 298 K, but our value of $F_c = 0.6$ gives a similar result. In a supplementary review, Baulch et al. (1982) suggest a slight temperature dependence for F_c, which would cause their suggested value to rise to $F_c = 0.85$ at 200 K.

7. $OH + NO$. The low-pressure limit rate constant has been reported by Anderson and Kaufman (1972), Stuhl and Niki (1972), Morley and Smith (1972), Westenberg and de Haas (1972), Anderson et al (1974), Howard and Evenson (1974), Harris and Wayne (1975), Atkinson et al (1975), Overend et al (1976), Anastasi and Smith (1978), and Burrows et al (1983). The general agreement is good, and the recommended value is a weighted average, with heavy weighting to the work of Anastasi and Smith. The reported high pressure limit rate constant is generally obtained from extrapolation. The recommended value is a weighted average of the reports in Anastasi and Smith (1978) and Anderson et al (1974). [Both cis and trans--HONO are expected to be formed.]

8. $OH + NO_2$. The low-pressure limit is from Anderson et al (1974), who report n = 2.5 (240 < T/K < 450); Howard and Evenson (1974): Anastasi and Smith (1976), who report n = 2.6 (220 < T/K < 550) and Wine et al (1979) who support these values over the range (247 < T/K < 352). The recommended value of n = 3.2 comes from $\langle\Delta E\rangle_{N_2}$ = 0.55 kcal mole^{-1}. (This value is consistent with the experiments.) Burrows et al (1983) confirm the value of k at 295 K. The high-pressure limit and T-dependence come from RRKM model of Smith and Golden (1978), although the error limits have been expanded to encompass m = 0. Robertshaw and Smith (1982) have measured k up to 8.6 atmospheres of CF_4. Their work suggests that k_∞ might be higher than suggested here (~50%). This might also be due to other causes (i.e., isomer formation or involvement of excited electronic states). Burkholder et al (1987) have shown that $HONO_2$ is the only isomer formed (yield = .75±$^{.25}_{.10}$). The recommendation here fits all data over the range of atmospheric interest.

9. $HO_2 + NO_2$. Recently Kurylo and Ouellette (1986) have remeasured the 300 K range constants. Kurylo and Ouellette (1987) have also remeasured the temperature dependence. The recommended values are taken from this latter reference wherein their data were combined with that of Sander and Peterson (1984). The recommended k_o(300 K) is consistent with Howard (1977). Other studies by Simonaitis and Heicklen (1978) and Cox and Patrick (1979) are in reasonable agreement with the recommendations.

10. $NO_2 + NO_3$. Data with N_2 as the bath gas from Kircher et al (1984), Croce de Cobos et al (1987a) (up to P = 5 atm), Smith et al (1985), Burrows et al (1985a), and Wallington et al (1987a) were used to obtain k_o^{300} and k_∞^{300}. Values from Croce de Cobos et al (1984) at pressures above 10 atm are 30% higher than the curve used herein. The values of n = 4.3 and m = 0.5 are from Kircher et al (1984). The study of Fowles et al (1982) is noted, but not used. Johnston et al (1986) have reviewed this reaction.

    Data for the reverse reaction have been obtained by Connell and Johnston (1979) and Viggiano et al (1981). (These two data sets are in reasonable agreement under overlapping conditions.) These data may be compared to the suggested parameters by multiplying by the recently redetermined equilibrium constant given in Table 3. The agreement is good. If the previous value of the equilibrium constant is used, the agreement is less good.

11. $Cl + NO$. Low-pressure limit from Lee et al (1978a), Clark et al (1966), Ashmore and Spencer (1959), and Ravishankara et al (1978). Temperature dependence from Lee et al (1978a) and Clark et al (1966).

12. $Cl + NO_2$. Low-pressure limit and T-dependence from Leu (1984a). (Assuming similar T-dependence in N_2 and He.) Leu (1984a) confirms the observation of Niki et al (1978c) that both ClONO and $ClNO_2$ are formed, with the former dominating. This has been explained by Chang et al (1979a), with detailed calculations in Patrick and Golden (1983). The temperature dependence is as predicted in Patrick and Golden (1983). Leu's results are in excellent agreement with those reported in Ravishankara et al (1988). The latter work extends to 200 torr and the high pressure limit was chosen to fit these measurements. The temperature dependence of the high pressure limit is estimated.

13. $Cl + O_2$. Nichovich et al (1989) measure k = (9±4) x 10^{-33} cm^6 molecule^{-2} s^{-1} at T = 187±6K in O_2. Using the methods described in Patrick and Golden (1983), but adjusting the thermochemistry of ClO_2 such that S^o_{298} = 64.3 cal mol^{-1} K^{-1} and $\Delta H_{f,298}$ = 23.3±0.6 kcal mol^{-1} (see Note 6 of Table 3), we calculate 5.4 x 10^{-33} cm^6 molecule^{-2} s^{-1} at T = 185 K with collisional efficiency of the bath gas taken from the formula $[\beta/1-\beta^{1/2}]$ = $\langle\Delta E\rangle/F_E$ kT and $\langle\Delta E\rangle$ ~0.5 kcal mole^{-1} (i.e., β_{185} = .42 and β_{300} = .30). Since O_2 may be particularly efficient for this process we use this calculation with broader error limits. The value from the calculation at 300 K (i.e., 2.7 x 10^{-33} cm^6 molecule^{-2} s^{-1}) compares with an older value of Nicholas and Norrish (1968) of 1.7 x 10^{-33} in an $N_2 + O_2$ mixture. The temperature dependence is from the calculation.

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14. Cl + CO. New Entry. From Nicovich et al (1990) who measured the process in N_2 for $185 \leq T/K \leq 260$.

15. Cl + C_2H_2. Brunning and Stief (1985) measured k from 210 to 361 K in Ar between 10 and 300 torr. Experiments in N_2 at 296 K were used to scale the low-pressure limiting rate constant. They report:

$$k_o = (1.0\pm0.2) \times 10^{-29} (T/300)^{-3.50\pm0.05}$$

$$k_\infty = (4.7\pm0.9) \times 10^{-11} (T/300)^{-2.63\pm0.05}$$

Wallington et al (1989) measured k at 295 K in air between 50 and 5800 torr. They report for a combination of their data and the 296 K, N_2 data of Brunning and Stief:

$$k_o = (6.1\pm0.8) \times 10^{-30}$$

$$k_\infty = (1.9\pm0.3) \times 10^{-10}$$

The values recommended here, place heavier weight on the data at pressures below an atmosphere. The temperature dependence is from Brunning and Stief with increased error limits. These values are compatible with earlier studies at Poulet et al (1973), Atkinson and Aschmann (1985), Lee and Rowland (1977) and Wallington et al (1988).

16. ClO + ClO. The values are taken from Sander et al (1989). They are consistent with a calculation of the type in Patrick and Golden (1983) using the entropy of $(ClO)_2$ determined by Cox and Hayman (1988). Hayman et al (1986) report a higher value at higher temperatures that is not consistent in the above sense. Other previous measurements, such as Cox and Derwent (1979), Basco and Hunt (1979) and Walker (1972) and Johnston et al (1969) range from 1-5 $\times 10^{-32}$ cm^6 s^{-1} with N_2 or O_2 as third bodies.

Unpublished work of Trolier et al (1989), when evaluated in the same fashion leads to:

$$k_o = (2.30\pm0.32) \times 10^{-32} (T/300)^{-3.4\pm0.4}$$

$$k_\infty = (1.93\pm0.28) \times 10^{-12} (T/300)^{-2.6\pm0.8}$$

They also report a possible zero pressure pathway. Their data is reasonably reproduced by the parameters recommended here.

17. ClO + NO_2. Several independent low-pressure determinations (Zahniser et al, 1977; Birks et al, 1977; Leu et al, 1977; Lee et al, 1982) of the rate of ClO disappearance via the ClO + NO_2 + M reaction are in excellent agreement and give an average $k_o(300)$ near 1.8 $\times 10^{-31}$ cm^6 s^{-1}. No product identification was carried out, and it was assumed that the reaction gave chlorine nitrate, $ClONO_2$. In contrast, direct measurements of the rate of thermal decomposition of $ClONO_2$ (Knauth, 1978; Schone et al, 1979), and recently Anderson and Fahey (1990), when combined with the accepted thermochemistry give a value lower by a factor of three. It is concluded that earlier measurements of the heat of formation are incorrect and the value 5.5 kcal $mole^{-1}$ evaluated from the kinetics by Anderson and Fahey (1989) is accepted.

Earlier explanations to the effect that the low-pressure ClO disappearance studies measured not only a reaction forming $ClONO_2$, but another channel forming an isomer, such as $OClNO_2$, ClOONO, or OClONO (Chang et al, 1979a; Molina et al, 1980a) are obviated by the above and work of Margitan (1983b), Cox et al (1984b), and Burrows et al (1985a) which indicates that there are no isomers of $ClONO_2$ formed. Wallington and Cox (1986) confirm current values, but are unable to explain the effect of OClO observed

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by both Molina et al (1980a) and themselves.

The high-pressure limit rate constants and their temperature dependence are from the model of Smith and Golden (1978). The recommended rate constants fit measured rate data for the disappearance of reactants (Cox and Lewis, 1979; Dasch et al, 1981). Data from Handwerk and Zellner (1984) indicate a slightly lower k_∞.

18. BrO + NO_2. Earlier measurements and 300 K from Sander et al (1981) are combined with recent work of Thorn et al (1989) who measured the rate constant at pressures from 16 to 800 torr of N_2 and at 268, 298, and 346 K.

The value of k_0 seems large and possible isomer formation cannot be ignored even though similar suggestions for ClO + NO_2 are not important.

19. F + O_2. A recent study by Pagsberg et al (1987) reports k_0 in Argon = 4.38 x 10^{-33} $(T/300)^{-1.2}$. This is in good agreement with earlier values of Smith and Wrigley (1980), Smith and Wrigley (1981), Shamonina and Kotov (1979), Arutyhonov et al (1976) and slightly lower than the values of Chen et al (1977) and Chegodaev et al (1978). Lyman and Holland (1988) report a slightly lower value in Ar and 298 K. We assume that $\beta_{Ar} = \beta_{N2}$ at all temperatures.

Pagsberg et al (1987), also determined the equilibrium constant and thus ΔH_f (FO_2). See Note 11 of Table 3. A calculation such as described in Patrick and Golden (1983), using the new value yields: $k_0 = 1.06$ x 10^{-33} $(T/300)^{-1.5}$ using $\beta_{N2} = 0.3$ (i.e., $<\Delta E> = 2$ kJ mol^{-1}). This is not good agreement.

20. F + NO. Parameters estimated from strong collision calculations with $<\Delta E>$ set at .42 kcal/mole^{-1}, yielding $\beta = 0.30$ at 300 K and $\beta = 0.38$ at 200 K.

21. F + NO_2. Experimental data of Fasano and Nogar (1983) were used to determine both the high and low pressure limits at 300 K. They fit their data to an expression such as recommended here.

Treatment of the data for this system requires knowledge of the relative stabilities of FNO_2 and FONO. Patrick and Golden (1983) assumed that the difference between these would be the same as between the $ClNO_2$ isomers. Thus, they concluded that $k^o_{300}(FNO_2) = 8.9$ x 10^{-31} and $k^o_{300}(FONO) = 2.4$ x 10^{-30}, and that FONO would be formed ~3 times more favorably than FNO_2. We have found an error of a factor of four in their calculations, which would predict $k^o_{300}(FONO) \simeq 1.06$ x 10^{-29}, and thus an overwhelming amount of FONO. The measured value is k ~1.06 x 10^{-30}, which is one-tenth of the predicted value.

A calculation at the MP-3/6-31G* level by Evleth (private communication, 1984) indicates that the FONO is much more than 10 kcal mol^{-1} less stable than FNO_2 and that its rate of formation can be ignored. Thus, we have k(exp) = k(FNO_2) = 1.06 x 10^{-30}.

The value of n = 2 is from Patrick and Golden, and the value of m is a rough estimate from similar reactions.

22. FO + NO_2. Low-pressure limit from strong collision calculation and $\beta = 0.33$. T-dependence from resultant $<\Delta E> = .52$ kcal mole^{-1}. High-pressure limit and T-dependence estimated. Once again (see Note 16) multiple channels could be important here, which would mean that the reaction between FO and NO_2 could be much faster, since these values consider only $FONO_2$ formation.

23. $CH_3 + O_2$. Low-pressure limit from Seltzer and Bayes (1983). (These workers determined the rate constants as a function of pressure in N_2, Ar, O_2, and He. Only the N_2 points were used directly in the evaluation, but the others are consistent.) Plumb and Ryan (1982b) report a value in He which is consistent within error limits with the work of Seltzer and Bayes. Pilling and Smith (1985) have measured this process in Ar (32-490 torr). Their low pressure limiting rate constant is consistent with this evaluation, but their high pressure value is a little low. Cobos et al (1985) have made measurements in Ar and N_2 from 0.25 to 150 atmospheres. They report parameters somewhat different than recommended here, but their data are reproduced well by the recommended values. The work of Laguna and Baughcum (1982) seems to be in the fall-off region. Results of Pratt and Wood (1984) in Ar are consistent with this recommendation, although the measurements are indirect. Their T-dependence is within our estimate. As can be seen from Patrick and Golden (1983), the above value leads to a very small β, ~.02, and thus temperature dependence is hard to calculate. The suggested value has been changed from the previous evaluation to accommodate the values of Kieffer et al (1987) who measure the process in Ar between 20 and 600 torr and in the range $334 \leq T/K \leq 582$. Ryan and Plumb (1984) suggest that the same type of calculation as employed by Patrick and Golden yields a reasonable value of β. We have not been able to reproduce their results. The high pressure rate constant fits the data of Cobos et al (1985). The temperature dependence is an estimate. (Data of van den Bergh and Callear (1971), Hochanadel et al (1977), Basco et al (1972), Washida and Bayes (1976), Laufer and Bass (1975), and Washida (1980) are also considered.) The fit to Keiffer et al (1987) is very good, suggesting that the temperature dependence for the high pressure limit is also reasonable.

24. $C_2H_5 + O_2$. New Entry. This recommendation is taken from IUPAC (1989).

25. $CH_3O_2 + NO_2$. Parameters from a reasonable fit to the temperature and pressure-dependent data in Sander and Watson (1980) and Ravishankara et al (1980a). The former reference reports their room-temperature data in the same form as herein, but they allow F_c to vary. They report:

$$k_o = 2.33 \times 10^{-30}, \quad k_\infty = 8 \times 10^{-12}, \quad F_c = 0.4$$

which is not a qualitatively different fit to the data at 300 K. The latter reference reports temperature dependence as:

$$k_o = 2.2 \times 10^{-30}(T/300)^{-2.5}, \quad k_\infty = 7 \times 10^{-12}(T/300)^{-3.5}, \quad F_c = 0.4.$$

These parameters are a better fit at all temperatures than those recommended here. We do not adopt them since they are not much better in stratospheric range, and they would require both a change in our $F_c = 0.6$ format, and the adoption of a quite large negative activation energy for k_∞.

The IUPAC (1989) recommendations are: $k_o = 2.3 \times 10^{-30}(T/300)^{-4}$, $k_\infty = 8 \times 10^{-12}$ and $F_c = e^{-T/327}$ yielding $F_c = .40$ at 300 K and .54 at 200 K. These values do not fit the data as well as the current recommendations. It is interesting to note that the data require a negative T-dependence for k_∞, similar to our $HO_2 + NO_2$ recommendation, and that the value of β at 300 K is ~.2.

A recent study of the reverse reaction by Zabel et al (1989) reports:

$$k_o/[N_2] = 9.0 \times 10^{-5} \exp(-80.6 \text{ kJ mole}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1};$$

$$k_\infty = 1.1 \times 10^{16} \exp(-87.8 \text{ kJ mole}^{-1}/RT) \text{ sec}^{-1}, \quad F_c = 0.4$$

The values recommended herein taken with the value of the equilibrium constant in Table 3, fit the data in Zabel et al (1989) very well.

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Destriau and Troe (1990) have fit the above data to:

$k_o/[N_2] = 2.5 \times 10^{-30} (T/298)^{-5.5}$, $k_\infty = 7.5 \times 10^{-12}$ independent of temperature, $F_c = 0.36$

26. $OH + SO_2$. Values of the rate constant as a function of pressure at 298 K from Leu (1982), Paraskevopoulos et al (1983), and Wine et al (1984b). The value of the low pressure limit is from Leu (1982), corrected for fall-off. The high pressure limit is from a fit to all the data.

The value of n comes from the above data combined with calculations such as those of Patrick and Golden (1983), except that the heat of formation of $HOSO_2$ is raised by 4 kcal mol^{-1}, as suggested by the work of Margitan (1984). The value of m is estimated. This is not a radical-radical reaction and is unlikely to have a positive value of m. The limit of m = -2 corresponds to a real activation energy of ~1 kcal mol^{-1}. Earlier data listed in Baulch et al (1980) and Baulch et al (1982) are noted. Recent work of Martin et al (1986) and Barnes et al (1986a) confirms the current evaluation.

27. $OH + C_2H_4$. Experimental data of Tully (1983), Davis et al (1975), Howard (1976), Greiner (1970a), Morris et al (1971), and Overend and Paraskevopolous (1977b) in helium, Atkinson et al (1977a) in argon, and Lloyd et al (1976) and Cox (1975) and Klein et al (1984) in nitrogen/oxygen mixtures, have been considered in the evaluation. This well-studied reaction is considerably more complex than most others in this table. The parameters recommended here fit exactly the same curve proposed by Klein et al (1984) at 298 K. Discrepancies remain and the effect of multiple product channels is not well understood. The temperature dependence of the low-pressure limit has not been determined experimentally. Calculations of the type in Patrick and Golden (1983) yield the recommended value. The high-pressure limit temperature dependence has been determined by several workers. Almost all obtain negative activation energies, the Zellner and Lorenz (1984) value being equivalent to m = +0.8 over the range (296 < T/K < 524) at about 1 atmosphere. Although this could theoretically arise as a result of reversibility, the equilibrium constant is too high for this possibility. If there is a product channel that proceeds with a low barrier via a tight transition state, a complex rate constant may yield the observed behavior. The actual addition process ($OH + C_2H_4$) may even have a small positive barrier. The recommended limits encompass the reported values.

28. $OH + C_2H_2$. The rate constant for this complex process has recently been re-examined by G. P. Smith et al (1984) in the temperature range from 228 to 1400 K, and in the pressure range 1 to 760 torr. Their analysis, which is cast in similar terms to those used here, is the source of the rate constants and temperature dependences at both limits. The negative value of m reflects the fact that their analysis includes a 1.2 kcal/mole barrier for the addition of OH to C_2H_2.

The data analyzed include those of Pastrana and Carr (1974), Perry et al (1977), Michael et al (1980), and Perry and Williamson (1982). Other data of Wilson and Westenberg (1967), Breen and Glass (1971), Smith and Zellner (1973), and Davis et al (1975) were not included. A recent study by Liu et al (1988) is in general agreement with the recommendation. Calculations of k_o via the methods of Patrick and Golden (1983) yield values compatible with those of Smith et al.

29. $CF_3 + O_2$. Caralp et al (1986) have measured the rate constant in N_2 between 1 and 10 torr. This supplants the value from Caralp and Lesclaux (1983). They recommend different parameters, but the data are well represented by the currently recommended values. Data of Ryan and Plumb (1982) are in agreement.

30. $CFCl_2 + O_2$. Values for both low- and high-pressure limits at 300 K are from Caralp and Lesclaux (1983). Temperature dependences are rough estimates based on similar reactions.

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31. $CCl_3 + O_2$. Values for both low- and high-pressure limits are from Ryan and Plumb (1984). They use the same format as recommended here and report:

$$k_o^{300}(He) = (5.8 \pm 0.6) \times 10^{-31}, \quad k_\infty^{300} = 2.5 \times 10^{-12} \text{ with } F = 0.25.$$

We find a good fit to their data using $F = 0.6$ to yield $k_o^{300}(He) = 4 \times 10^{-31}$, keeping $k_\infty^{300} = 2.5 \times 10^{-12}$.

The recommended value of $k_o^{300}(N_2)$ is 2.5 times the value in He.

Temperature dependences are rough estimates based on similar reactions. A value of $k_\infty^{300} = 5 \times 10^{-12}$ has been reported by Cooper et al (1980).

32. $CFCl_2O_2 + NO_2$. Based on experiments in O_2 of Caralp et al (1988), who suggest a somewhat different fitting procedure, but the values recommended here fit the data just as well. Destriau and Troe (1990) use yet a different fitting procedure that does not represent the data quite as well as that recommended herein.

33. $CF_3O_2 + NO_2$. New Entry. Based on experiments in O_2 of Caralp et al (1988), who suggest a somewhat different fitting procedure, but the values recommended here fit the data just as well. Destriau and Troe (1990) use yet a different fitting procedure that does not represent the data quite as well as that recommended herein.

34. $CCl_3O_2 + NO_2$. New Entry. Based on experiments in O_2 of Caralp et al (1988), who suggest a somewhat different fitting procedure, but the values recommended here fit the data just as well. Destriau and Troe (1990) use yet a different fitting procedure that does not represent the data quite as well as that recommended herein.

35. $HS + NO$. Data and analysis are from the recent work of Black et al (1984). The temperature dependence of k_∞ has been estimated.

36. $Na + O_2$. A recent study by Plane and Rajasekhar (1989) finds $k_o = (2.9 \pm 0.7) \times 10^{-30}$ at 300 K with $n = 1.30 \pm .04$. They also estimate $k_\infty \sim 6 \times 10^{-10}$ with a slight positive temperature dependence. The k_o value is about 60% higher than that of Silver et al (1984b). The recommended value is an average of the two studies.

37. $NaO + O_2$. Ager and Howard (1986) have measured the low-pressure limit at room temperature in several bath gases. Their value in N_2 is used in the recommendation. They performed a Troe calculation as per Patrick and Golden (1983) to obtain collision efficiency and temperature dependence. They obtained a high-pressure limit rate constant by use of a simple model. The temperature dependence is estimated.

38. $NaO + CO_2$. Ager and Howard (1986) have measured the rate constant for this process in the "fall-off" regime. Their lowest pressures are very close to the low-pressure limit. The temperature dependence is an estimate. Ager and Howard calculate the high-pressure rate constant from a simple model. The temperature dependence is an estimate.

39. $NaOH + CO_2$. Ager and Howard (1987b) have measured the low-pressure limiting rate constant. The temperature dependence is an estimate. Ager and Howard have calculated the high-pressure limit using a simple model. The temperature dependence is an estimate.

EQUILIBRIUM CONSTANTS

Format

Some of the three-body reactions in Table 2 form products which are thermally unstable at atmospheric temperatures. In such cases the thermal decomposition reaction may compete with other loss processes, such as photo-dissociation or radical attack. Table 3 lists the equilibrium constants, K(T), for eleven reactions which may fall into this category. The table has three column entries, the first two being the parameters A and B which can be used to express K(T):

$$K(T)/cm^3 \ molecule^{-1} = A \ exp(B/T) \quad (200 < T < 300 \ K)$$

The third column entry in Table 3 is the calculated value of K at 298 K.

The data sources for K(T) are described in the individual notes to Table 3. When values of the heats of formation and entropies of all species are known at the temperature T, we note that:

$$log[K(T)/cm^3 \ molecule^{-1}] = \frac{\Delta S_T^o}{2.303R} - \frac{\Delta H_T^o}{2.303RT} + log \ T - 21.87$$

where the superscript "o" refers to a standard state of one atmosphere. In some cases K values were calculated from this equation, using thermochemical data. In other cases the K values were calculated directly from kinetic data for the forward and reverse reactions. When available, JANAF values were used for the equilibrium constants. The following equations were then used to calculate the parameters A and B:

$$B/^oK = 2.303 \ [log \ \frac{K_{200}}{K_{300}}] \ (\frac{300 \ x \ 200}{300 - 200})$$

$$= 1382 \ log(K_{200}/K_{300})$$

$$log \ A = log \ K(T) - B/2.303 \ T$$

Table 3. Equilibrium Constants

Reaction	$A/cm^3\ molecule^{-1}$	$B\pm\Delta B/°K$	$K_{eq}(298\ K)$	$f(298\ K)^a$	Note
$HO_2 + NO_2 \rightarrow HO_2NO_2$	2.1×10^{-27}	$10,900\pm1,000$	1.6×10^{-11}	5	1
$NO + NO_2 \rightarrow N_2O_3$	3.0×10^{-27}	$4,700\pm100$	2.1×10^{-20}	2	2
# $NO_2 + NO_2 \rightarrow N_2O_4$	5.9×10^{-29}	$6,600\pm250$	2.5×10^{-19}	2	3
* $NO_2 + NO_3 \rightarrow N_2O_5$	4.0×10^{-27}	$10,930\pm500$	3.4×10^{-11}	1.5	4
$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	1.3×10^{-28}	$11,200\pm1,000$	2.7×10^{-12}	2	5
* $Cl + O_2 \rightarrow ClOO$	5.7×10^{-25}	$2,500\pm750$	2.5×10^{-21}	2	6
$ClO + O_2 \rightarrow ClO\cdot O_2$	$<2.9\times10^{-26}$	$<5,000\pm1,500$	$<5.6\times10^{-19}$		7
# $Cl + CO \rightarrow ClCO$	1.6×10^{-25}	$4,000\pm500$	1.1×10^{-19}	5	8
* $ClO + ClO \rightarrow Cl_2O_2$	3.0×10^{-27}	$8,450\pm850$	6.2×10^{-15}	2	9
# $ClO + OClO \rightarrow Cl_2O_3$	1.6×10^{-27}	$7,200\pm1,400$	5.0×10^{-17}	10	10
* $F + O_2 \rightarrow FOO$	3.2×10^{-25}	$6,100\pm1,200$	2.5×10^{-16}	10	11

$K_{eq}/cm^3\ molecule^{-1} = A\ exp(B/T)\ [200 < T/K < 300]$

[a] $f(298\ K)$ is the uncertainty factor in K_{eq} at 298 K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298\ K)\ exp(\Delta B\ |\frac{1}{T} - \frac{1}{298}|)$.

* Indicates a change from the previous Panel evaluation.

& Indicates a change in the Note.

# Indicates a new entry in the Table.

1. $HO_2 + NO_2$. The value was obtained by combining the data of Sander and Peterson (1984) for the rate constant of the reaction as written and that of Graham et al (1977) for the reverse reaction.

   From the equilibrium constant, it may be inferred that the thermal decomposition of HO_2NO_2 is unimportant in the stratosphere, but is important in the troposphere.

2. $NO + NO_2$. The data are from JANAF. This process is included because a recent measurement of the rate constant by Smith and Yarwood (1986) shows that it is too slow to be an important rate process, but there will be some equilibrium concentration present.

3. $NO_2 + NO_2$. New Entry. The data are from JANAF. Recent rate data for this process are reported by Brunning et al (1988), Borrell et al (1988), and Gozel et al (1984).

4. $NO_2 + NO_3$. Note changed from JPL 87-41. The recommendation is an average of the temperature dependence data of Burrows et al (1985c) and Cantrell et al (1988), and the room temperature data of Tuazon et al (1983) and Perner et al (1985). The entry in Table 3 is not exactly equivalent to the ratio of the forward rate constant from Table 2 and the reverse rate constant from the data of Connell and Johnston (1979) and Viggiano et al (1981). However, there is agreement within experimental error.

5. $CH_3O_2 + NO_2$. Thermochemical values at 300 K for $CH_3O_2NO_2$ and CH_3O_2 are from Baldwin (1982).

   In the absence of data, ΔH^o and ΔS^o were assumed to be independent of temperature. Bahta et al (1982) have measured k(dissociation) at 263 K. Using the values of k(recombination) suggested in this evaluation, they compute $K(263) = (2.68 \pm 0.26) \times 10^{-10}$ cm^3. Our values predict 3.94×10^{-10} cm^3, in good agreement.

   Zabel et al (1989) have measured k(dissociation) as a function of pressure and temperature (see Note 25, Table 2). Their values are in good agreement with Bahta et al (1982) and would lead to $A = 5.2 \times 10^{-28}$ and $B = 10,766$. This is sufficiently close to the value in Table 3 to forego any change, but the uncertainty has been reduced.

6. $Cl + O_2$. Nicovich et al (1989) measure $K = 5.30 \times 10^{-19}$ cm^3 $molecule^{-1}$ at 185 K. Using known thermochemistry for Cl and O_2 and computed values for ClO_2, $\Delta H_{f,298}(ClO_2) = 23.3 \pm 0.6$ kcal $mole^{-1}$ is obtained. [The value of $S^o_{298}(ClO_2) = 64.3$ cal $mole^{-1}$ K^{-1} used, is computed from a structure with an 105° bond angle and Cl-O and O-O bond lengths of 1.73 and 1.30Å respectively. Frequencies of 1441, 407 and 373 cm^{-1} are from Arkell and Schwager (1967). Symmetry number is 1 and degeneracy is 2.]

7. $ClO + O_2$. Zellner (private communication, 1982) suggests $K < 12$ atm^{-1} and $\Delta H \geq -11$ kcal/mol. The corresponding value of A leads to $S^o 300(ClO \cdot O_2) \sim 73$ cal mol^{-1} K^{-1}. A higher value of K has been proposed by Prasad (1980), but it requires $S^o(ClO \cdot O_2)$ to be about 83 cal mol^{-1} K^{-1}, which seems unreasonably high. Carter and Andrews (1981) found no experimental evidence for $ClO \cdot O_2$ in matrix experiments.

8. $Cl + CO$. New Entry. From Nicovich et al (1989) who measured both k and K between 185 and 260 K in N_2. They report $\Delta H_{f,298}(ClCO) = -5.2 \pm 0.7$ kcal $mole^{-1}$.

9. $ClO + ClO$. The value is from Cox & Hayman (1988). The corresponding entropy of the dimer is 74 cal mol^{-1} K^{-1} and $\Delta H_f = 31.5$ kcal mol^{-1}. Previous work of Cox and Derwent (1979) and Hayman et al (1986) is noted.

10. ClO + OClO. New Entry. Data is taken from Hayman and Cox (1989). They deduce ΔH_f (Cl_2O_3) = 34±3 kcal mole^{-1} and $S^o(Cl_2O_3)$ = 80+12 cal mole^{-1} ^{o}K^{-1}.

11. F + O_2. Calculated from JANAF thermochemical values except for $\Delta H_{f,298}(FO_2)$ = 6.24±0.5 kcal mole^{-1}. The latter was taken from Pagsberg et al (1987). This direct measurement, which falls between the earlier disputed values would seem to settle that controversy, but (see Note 19 of Table 2) the calculated value of k_o is not in good agreement with the experiment.

PHOTOCHEMICAL DATA

Discussion of Format and Error Estimates

In Table 4 we present a list of photochemical reactions considered to be of stratospheric interest. The absorption cross sections of O_2 and O_3 largely determine the extent of penetration of solar radiation into the stratosphere and troposphere. Some comments and references to these cross sections are presented in the text, but only a sample of the data is listed here. (See, for example, WMO Report #11, 1982; WMO-NASA, 1985.) The photodissociation of NO in the O_2 Schumann-Runge band spectral range is another important process requiring special treatment and is not discussed in this evaluation (see, for example, Frederick and Hudson, 1979; Allen and Frederick, 1982; and WMO Report #11, 1982).

For some other species having highly structured spectra, such as CS_2 and SO_2, some comments are given in the text, but the photochemical data are not presented. The species CH_2O, NO_2, NO_3, ClO, BrO, and OClO also have complicated spectra, but in view of their importance for atmospheric chemistry a sample of the data is presented in the evaluation; for more detailed information on their high-resolution spectra and temperature dependence, the reader is referred to the original literature.

Table 5 gives recommended reliability factors for some of the more important photochemical reactions. These factors represent the combined uncertainty in cross sections and quantum yields, taking into consideration the atmospherically important wavelength regions, and they refer to the total dissociation rate regardless of product identity (except in the case of $O(^1D)$ production from photolysis of O_3).

The absorption cross sections are defined by the following expression of Beer's Law:

$$I = I_0 exp(-\sigma nl),$$

where I_0 and I are the incident and transmitted light intensity, respectively; σ is the absorption cross section in cm^2 molecule^{-1}; n is the concentration in molecule cm^{-3}, and l is the pathlength in cm. The cross sections are room temperature values at the specific wavelengths listed in the tables, and the expected photodissociation quantum yields are unity, unless otherwise stated.

$O_2 + h\nu \rightarrow O + O$
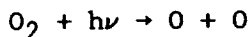
The photodissociation of molecular oxygen in the stratosphere is due primarily to absorption of solar radiation in the 200-220 nm wavelength region, i.e., within the Herzberg continuum. The 185-200 nm region--the O_2 Schumann-Runge band spectral range--is also very important, since solar radiation penetrates efficiently into the stratosphere at those wavelengths.

Table 4. Photochemical Reactions of Stratospheric Interest

& O_2 + hν → O + O

& O_3 + hν → O_2 + O

* O_3 + hν → O_2 + O(^{1}D)

* HO_2 + hν → products

H_2O + hν → H + OH   (1)

* H_2O_2 + hν → OH + OH

NO + hν → N + O

* NO_2 + hν → NO + O

* NO_3 + hν → products

& N_2O + hν → N_2 + O(^{1}D)

& N_2O_5 + hν → products

NH_3 + hν → NH_2 + H   (1)

HNO_2 + hν → OH + NO

& HNO_3 + hν → OH + NO_2

* HNO_4 + hν → products

Cl_2 + hν → Cl + Cl

* ClO + hν → Cl + O

ClOO + hν → products

OClO + hν → O + ClO

ClO_3 + hν → products

* Cl_2O_2 + hν → products

HCl + hν → H + Cl

* HOCl + hν → OH + Cl

ClNO + hν → Cl + NO

$ClNO_2$ + hν → products

ClONO + hν → products

& $ClONO_2$ + hν → products

CCl_4 + hν → products

CCl_3F + hν → products

CCl_2F_2 + hν → products

* $CHClF_2$ + hν → products

CH_3Cl + hν → products

CH_3CF_2Cl + hν → products

CF_3CHCl_2 + hν → products

CF_3CHFCl + hν → products

CH_3CFCl_2 + hν → products

CH_3CCl_3 + hν → products

* $CBrF_3$ + hν → products

CF_2Br_2 + hν → products

* $CBrClF_2$ + hν → products

CF_2BrCF_2Br + hν → products

CF_4 + hν → products

C_2F_6 + hν → products

SF_6 + hν → products

CCl_2O + hν → products

CClFO + hν → products

CF_2O + hν → products

* BrO + hν → Br + O

$BrONO_2$ + hν → products

HF + hν → H + F

CO + hν → C + O   (1)

CO_2 + hν → CO + O   (1)

CH_4 + hν → products   (2)

CH_2O → products

* CH_3OOH + hν → products

HCN + hν → products

& CH_3CN + hν → products

SO_2 + hν → SO + O

OCS + hν → CO + S

H_2S + hν → HS + H   (2)

CS_2 + hν → products

NaCl + hν → Na + Cl

NaOH + hν → Na + OH

---

(1) Hudson and Kieffer (1975)

(2) Turco (1975)

New entry

* Indicates a change in the recommendation from the previous evaluation.

& Indicates a change in the note.

Table 5. Combined Uncertainties for Cross Sections and
Quantum Yields

Species	Uncertainty
O_2 (Schumann-Runge bands)	1.4
O_2 (Continua)	1.3
O_3	1.1
$O_3 \rightarrow O(^1D)$	1.4
NO_2	1.3
NO_3	2.0
N_2O	1.2
N_2O_5	2.0
H_2O_2	1.4
HNO_3	1.3
HO_2NO_2	2.0
CH_2O	1.4
HCl	1.1
$HOCl$	1.4
$ClONO_2$	1.3
CCl_4	1.1
CCl_3F	1.1
CCl_2F_2	1.1
CH_3Cl	1.1
CF_2O	2.0
CH_3OOH	1.8
$BrONO_2$	1.4
CF_3Br	2.0
CF_2ClBr	3.0
CF_2Br_2	3.0
$C_2F_4Br_2$	3.0

Frederick and Mentall (1982) and Herman and Mentall (1982) have estimated O_2 absorption cross sections from balloon measurements of solar irradiance in the stratosphere. The latter authors find the cross sections in the 200-210 nm range to be ~35% smaller than the smallest of the older laboratory results, which are those of Shardanand and Prasad Rao (1977). There are three recent laboratory studies (Johnston et al, 1984; Chueng et al, 1984; Jenouvrier et al, 1986) which confirm the lower values obtained from solar irradiance measurements. There is also, however, a study of the penetration of stellar UV radiation into the stratosphere which agrees better with the higher O_2 cross section values (Pirre et al, 1984).

The attenuation of solar radiation in the Schumann-Runge wavelength region is a problem requiring special treatment due to the rotational structure of the bands; see, for example, Nicolet and Peetermans (1980); Frederick and Hudson (1980); and Allen and Frederick (1982). The effective O_2 cross sections obtained from solar irradiance measurements in the stratosphere by Herman and Mentall (1982) are in good agreement between 187 and 195 nm with the values reported by Allen and Frederick (1982), which were obtained by an empirical fit to the effective cross sections appropriate for stratospheric conditions. Between 195 and 200 nm the fit yielded values which are somewhat larger than those estimated by Herman and Mentall.

The studies of the penetration of solar radiation in the atmosphere in the Schumann-Runge wavelength region have been based so far on laboratory measurements of cross sections which were affected by instrumental parameters due to insufficient spectral resolution. Yoshino et al (1983) have reported high resolution O_2 cross section measurements at 300 K, between 179 and 202 nm, obtaining presumably the first set of results which is independent of the instrumental width. The Schumann-Runge cross sections are temperature-dependent, so that additional studies will be required in order to carry out detailed atmospheric modeling calculations. Furthermore, for estimates of the solar irradiance in the stratosphere the cross section values which need to be accurately known are those at the wings of the rotational lines and in the underlying continuum, and these are several orders of magnitude smaller than the peak values. Additional factors that need to be considered are the enhancement in solar absorption by O_2 due to the formation of "O_2 dimer" and collisions with N_2. The "O_2 dimer" may not be real and the enhancement in absorption may be due to relaxation of the selection rules for the electronic transitions during collision with another molecule. The "O_2 dimer" may lead to direct production of O_3 and O atoms, which is no different in the atmosphere than dissociation of O_2 to two O atoms. The Mainz group (Horowitz et al, 1988; 1989a; 1989b) have most recently investigated these pathways and should be consulted for further information. Lastly, the "O_2 dimer" will appear as a distinct absorption feature in long path uv-visible measurements in the atmosphere.

$$O_3 + h\nu \rightarrow O + O_2$$
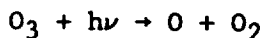
The O_3 absorption cross sections and their temperature dependence have been remeasured recently by several groups. For a review see WMO-NASA, 1985; Table 6 lists a sample of the data taken from this review, namely the 273 K cross section values averaged over the wavelength intervals commonly employed

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in modeling calculations, except for the wavelength range 185 to 225 nm, where the present recommendation incorporates the averaged values from the recent work of Molina and Molina (1986); the older values were based on the work of Inn and Tanaka (1953). The temperature effect is negligible for wavelengths shorter than ~260 nm. Recent work by Mauersberger et al (1986, 1987) yields a value of 1137 x 10^{-20} cm^2 for the cross section at 253.7 nm, the mercury line wavelength; it is about 1% smaller than the commonly accepted value of 1147 x 10^{-20} cm^2 reported by Hearn (1961), and about 2% smaller than the value obtained by Molina and Molina (1986), 1157 x 10^{-20} cm^2; see also Barnes and Mauersberger (1987). The reason for the small discrepancy, which appears to be beyond experimental precision, is unclear. Cacciani et al (1989) reported measurements of the ozone cross sections in the wavelength range from 339 to 355 nm, in reasonable agreement with the present recommendation.

Table 6. Absorption Cross Sections of O_3 at 273 K

λ (nm)	$10^{20}\sigma(cm^2)$ average	λ (nm)	$10^{20}\sigma(cm^2)$ average
175.439-176.991	81.1	238.095-240.964	797
176.991-178.571	79.9	240.964-243.902	900
178.571-180.180	78.6	243.902-246.914	1000
180.180-181.818	76.3	246.914-250.000	1080
181.818-183.486	72.9	250.000-253.165	1130
183.486-185.185	68.8	253.165-256.410	1150
185.185-186.916	62.2	256.410-259.740	1120
186.916-188.679	57.6	259.740-265.158	1060
188.679-190.476	52.6	263.158-266.667	965
190.476-192.308	47.6	266.667-270.270	834
192.308-194.175	42.8	270.270-273.973	692
194.175-196.078	38.3	273.973-277.778	542
196.078-198.020	34.7	277.778-281.690	402
198.020-200.000	32.3	281.690-285.714	277
200.000-202.020	31.4	285.714-289.855	179
202.020-204.082	32.6	289.855-294.118	109
204.082-206.186	36.4	294.118-298.507	62.4
206.186-208.333	43.4	298.507-303.030	34.3
208.333-210.526	54.2	303.030-307.692	18.5
210.526-212.766	69.9	307.692-312.5	9.80
212.766-215.054	92.1	312.5-317.5	5.01
215.054-217.391	119	317.5-322.5	2.49
217.391-219.780	155	322.5-327.5	1.20
219.780-222.222	199	327.5-332.5	0.617
222.222-224.719	256	332.5-337.5	0.274
224.719-227.273	323	337.5-342.5	0.117
227.273-229.885	400	342.5-347.5	0.0588
229.885-232.558	483	347.5-352.5	0.0266
232.558-235.294	579	352.5-357.5	0.0109
235.294-238.095	686	357.5-362.5	0.00549

The quantum yields for $O(^1D)$ production, $\Phi(O^1D)$, for wavelengths near 310 nm, i.e., the energetic threshold or fall-off region, have been measured mostly relative to quantum yields for wavelengths shorter than 300 nm, which were assumed to be unity. There are several studies which indicate that this assumption is not correct: Fairchild et al (1978) observed approximately 10% of the primary photolysis products in the ground state channel, that is, $\Phi(O^3P)$ ~0.1, at 274 nm; Sparks et al (1980) also report $\Phi(O^3P)$ ~0.1, at 266 nm; according to Brock and Watson (1980b) $\Phi(O^1D) = 0.88$ at 266 nm; Amimoto et al (1980) report $\Phi(O^1D) = 0.85$ at 248 nm, and Wine and Ravishankara (1982) measured directly $\Phi(O^1D) = 0.9$ at 248 nm. There are also some indications that $\Phi(O^1D)$ decreases slightly between 304 and 275 nm (see Brock and Watson, 1980a,b).

The recommendation for the quantum yields in the fall-off region has been modified to represent more accurately the high resolution laser data of Arnold et al (1977), Brock and Watson (1980b), and Trolier and Wiesenfeld (1988). An exception is that the "tail" sometimes seen in the laser experiments at longer wavelengths has been eliminated, on the grounds that it is not reproduced in the monochromator experiments and may be an artifact. This question requires further study. Also needed are laser experiments at lower temperatures. Temperature dependence in the present recommendation is based on the monochromator experiments of Moortgat and Kudzus (1978).

Table 7. Mathematical Expression for $O(^1D)$ Quantum Yields, Φ, in the Photolysis of O_3 in the Wavelength Region 305 to 320 nm.

$$\Phi(\lambda,T) = a_0(\tau) + a_1(\tau)x + a_2(\tau)x^2 + a_3(\tau)x^3 +$$
$$a_4(\tau)x^4 + a_5(\tau)x^5 + a_6(\tau)x^6$$

where $x = (\lambda-305)$ and $\tau = (298-T(K))$ and

$a_0 = .94932 - 1.7039 \cdot 10^{-4} \, \tau + 1.4072 \cdot 10^{-6} \, \tau^2$

$a_1 = -2.4052 \cdot 10^{-2} + 1.0479 \cdot 10^{-3} \, \tau - 1.0655 \cdot 10^{-5} \, \tau^2$

$a_2 = 1.8771 \cdot 10^{-2} - 3.6401 \cdot 10^{-4} \, \tau - 1.8587 \cdot 10^{-5} \, \tau^2$

$a_3 = -1.454 \cdot 10^{-2} - 4.7787 \cdot 10^{-5} \, \tau + 8.1277 \cdot 10^{-6} \, \tau^2$

$a_4 = 2.3287 \cdot 10^{-3} + 1.9891 \cdot 10^{-5} \, \tau - 1.1801 \cdot 10^{-6} \, \tau^2$

$a_5 = -1.4471 \cdot 10^{-4} - 1.7188 \cdot 10^{-6} \, \tau + 7.2661 \cdot 10^{-8} \, \tau^2$

$a_6 = 3.183 \cdot 10^{-6} + 4.6209 \cdot 10^{-8} \, \tau - 1.6266 \cdot 10^{-9} \, \tau^2$

If $\phi(\lambda,T) < 0.02$ then let $\phi(\lambda,T) = 0$. For $\lambda < 305$ nm, $\phi(\lambda,T) = 0.95$. For $\lambda > 320$ nm, $\phi(\lambda,T) = 0$. Expression is valid for the temperature range 220-300 K.

$HO_2 + h\nu \rightarrow OH + O$
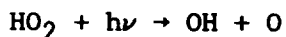
The absorption cross sections of the hydroperoxyl radical, HO_2, in the 200-250 nm region have been measured at room temperature by Paukert and Johnston (1972), Hochanadel et al (1972; 1980), Cox and Burrows (1979), McAdam et al (1987), and Kurylo et al (1987a); and by Sander et al (1982) at 227.5 nm.

There are significant discrepancies in the shape of the spectrum as well as in the absolute cross section values; at 227.5 nm, the value ranges from 250 to 309 x 10^{-20} cm^2/molecule, the average of all measurements being 269 x 10^{-20} cm^2/molecule.

Table 8 lists the recommended cross sections, which are computed from the mean of the five sets of reported values. This recommendation is given here merely to indicate that photolysis of HO_2 in the stratosphere and troposphere is not an important process and can be neglected. However, for chemical kinetics studies the simple average presented here needs not be the best choice and the most suitable cross section values to be used should be considered on a case-by-case basis.

Lee (1982) has detected $O(^1D)$ as a primary photodissociation product at 193 and at 248 nm, with a quantum yield which is about 15 times larger at the longer wavelength. The absolute quantum yield for $O(^1D)$ production has not been reported yet.

Table 8. Absorption Cross Sections of HO_2

λ(nm)	$10^{20}\sigma$(cm^2)
200	440
210	430
220	360
230	245
240	120
250	60

$H_2O_2 + h\nu \rightarrow OH + OH$
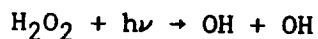
The recommended 298 K absorption cross section values, listed in Table 9, are the mean of the data of Lin et al (1978b), Molina and Molina (1981), Nicovich and Wine (1988), and Vaghjiani and Ravishankara (1989). Molina and Molina (1981) supersedes the earlier results of Molina et al (1977a). Nicovich and Wine measured the cross sections at $\lambda \geq 230$ relative to the values at 202.6, $\sigma = 4.32 \times 10^{-19}$ cm^2, and at 228.8 nm, $\sigma = 1.86 \times 10^{-19}$ cm^2. The values are within 2% of the recommended value.

Table 9. Absorption Cross Sections of H_2O_2 Vapor

λ (nm)	$10^{20}\sigma$ (cm^2)		λ (nm)	$10^{20}\sigma$ (cm^2)	
	298 K	355 K		298 K	355 K
190	67.2		270	3.3	3.5
195	56.4		275	2.6	2.8
200	47.5		280	2.0	2.2
205	40.8		285	1.5	1.6
210	35.7		290	1.2	1.3
215	30.7		295	0.90	1.0
220	25.8		300	0.68	0.79
225	21.7		305	0.51	0.58
230	18.2	18.4	310	0.39	0.46
235	15.0	15.2	315	0.29	0.36
240	12.4	12.6	320	0.22	0.27
245	10.2	10.8	325	0.16	0.21
250	8.3	8.5	330	0.13	0.17
255	6.7	6.9	335	0.10	0.13
260	5.3	5.5	340	0.07	0.10
265	4.2	4.4	345	0.05	0.06
			350	0.04	0.05

Nicovich and Wine have measured the temperature dependence of this cross section. They expressed the measured cross section as the sum of two components; one, σ_1, due to absorption from H_2O_2 which has the 0-0 stretch excited, and the other, σ_0, due to absorption by ground state molecules. For atmospheric calculations the expression given in Table 10 may be used. The photodissociation quantum yield is believed to be unity. At and above 248 nm, the major photodissociation process is that leading to OH, i.e., the quantum yield for OH production is 2 (Vaghjiani and Ravishankara, 1990).

Table 10. Mathematical Expression for Absorption Cross Sections of H_2O_2 as a Function of Temperature

$$10^{21}\, \sigma(\lambda,T) = \chi \sum_{n=0}^{7} A_n \lambda^n + (1 - \chi) \sum_{n=0}^{4} B_n \lambda^n$$

Where T: temperature Kelvin; λ: nm; $\chi = [1 + \exp\ (-1265/T)]^{-1}$

$A_0 = 6.4761 \times 10^4$ $B_0 = 6.8123 \times 10^3$

$A_1 = -9.2170972 \times 10^2$ $B_1 = -5.1351 \times 10^1$

$A_2 = 4.535649$ $B_2 = 1.1522 \times 10^{-1}$

$A_3 = -4.4589016 \times 10^{-3}$ $B_3 = -3.0493 \times 10^{-5}$

$A_4 = -4.035101 \times 10^{-5}$ $B_4 = -1.0924 \times 10^{-7}$

$A_5 = 1.6878206 \times 10^{-7}$

$A_6 = -2.652014 \times 10^{-10}$

$A_7 = 1.5534675 \times 10^{-13}$

Range 260-350 nm;   200-400 K

$$NO_2 + h\nu \rightarrow NO + O$$
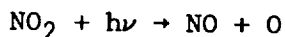
The previous recommendation for the absorption cross sections of nitrogen dioxide was taken from the work of Bass et al (1976). More recent measurements have been reported by Schneider et al (1987), at 298 K, for the wavelength range from 200 to 700 nm; and by Davidson et al (1988), from 270 to 420 nm, in the 232-397 K temperature range. At room temperature the agreement between these three sets of measurements is good; within 5% between 305 and 345 nm, and within 10% at the longer wavelengths. The agreement is poor below room temperature, as well as at the shorter wavelengths. A possible cause for the discrepancies is the presence of N_2O_4. The corrections needed to account for the presence of this species are largest around 200 nm, where it absorbs strongly. The corrections are also large at the lowest temperatures, because a significant fraction of the NO_2 forms N_2O_4. On the other hand, there is no error apparent in the corrections carried out by Bass et al, so that the reason for the discrepancy is not clear.

Table 11 lists the recommended absorption cross sections, averaged over the wavelength intervals used for atmospheric photodissociation calculations. For the wavelength range from 200 to 274 nm the values are taken from Schneider et al (1987); in this range the temperature effect is negligible. For the 274 to 420 nm region the temperature-dependent values are taken from Davidson et al (1988).

The earlier recommendation for quantum yields was based on the work of Harker et al (1977) and of Davenport (1978) for the atmospherically-important 375-470 nm region. The work by Gardner et al (1987) yields values which are in much better agreement with the values reported earlier by Jones and Bayes (1973). The recommended quantum yield values, listed in Table 12, are in agreement with the recommendation of Gardner et al (1987); they are based on a smooth fit to the data of Gardner et al (1987) for the wavelength range from 334 to 404 nm; Harker et al (1977) for 397-420 nm (corrected for cross sections); Davenport (1978) for 400-420 nm; and Jones and Bayes (1973) for 297-412 nm. Direct measurements of the solar photodissociation rate of NO_2 in the troposphere by Parrish et al (1988) and by Shetter et al (1988) agree better with theoretical estimates based on this recommendation than with the earlier one.
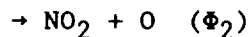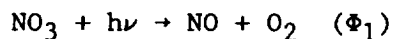
Table 11.   Absorption Cross Sections of NO_2

λ (nm)	10^{20} σ, average at 25°C cm^2 molecule^{-1}	λ (nm)	$10^{20}\sigma$, average at 0°C (cm^2 molecule^{-1})	10^{22} a* (cm^2 molecule^{-1} degree^{-1})
202.02 - 204.08	41.45	273.97 - 277.78	5.03	0.075
204.08 - 206.19	44.78	277.78 - 281.69	5.88	0.082
206.19 - 208.33	44.54	281.69 - 285.71	7.00	-0.053
208.33 - 210.53	46.41	285.71 - 289.85	8.15	-0.043
210.53 - 212.77	48.66	289.85 - 294.12	9.72	-0.031
212.77 - 215.06	48.18	294.12 - 298.51	11.54	-0.162
215.06 - 217.39	50.22	298.51 - 303.03	13.44	-0.284
217.39 - 219.78	44.41	303.03 - 307.69	15.89	-0.357
219.78 - 222.22	47.13	307.69 - 312.50	18.67	-0.536
222.22 - 224.72	37.72	312.5 - 317.5	21.53	-0.686
224.72 - 227.27	39.29	317.5 - 322.5	24.77	-0.786
227.27 - 229.89	27.40	322.5 - 327.5	28.07	-1.105
229.89 - 232.56	27.78	327.5 - 332.5	31.33	-1.355
232.56 - 235.29	16.89	332.5 - 337.5	34.25	-1.277
235.29 - 238.09	16.18	337.5 - 342.5	37.98	-1.612
238.09 - 240.96	8.812	342.5 - 347.5	40.65	-1.890
240.96 - 243.90	7.472	347.5 - 352.5	43.13	-1.219
243.90 - 246.91	3.909	352.5 - 357.5	47.17	-1.921
246.91 - 250.00	2.753	357.5 - 362.5	48.33	-1.095
250.00 - 253.17	2.007	262.5 - 367.5	51.66	-1.322
253.17 - 256.41	1.973	367.5 - 372.5	53.15	-1.102
256.41 - 259.74	2.111	372.5 - 377.5	55.08	-0.806
259.74 - 263.16	2.357	377.5 - 382.5	56.44	-0.867
263.16 - 266.67	2.698	382.5 - 387.5	57.57	-0.945
266.67 - 270.27	3.247	387.5 - 392.5	59.27	-0.923
270.27 - 273.97	3.785	392.5 - 397.5	58.45	-0.738
		397.5 - 402.5	60.21	-0.599
		402.5 - 407.5	57.81	-0.545
		407.5 - 412.5	59.99	-1.129
		412.5 - 417.5	56.51	0.001
		417.5 - 422.5	58.12	-1.208

*The quantity a is the temperature coefficient of σ as defined in the equation $\sigma(t) = \sigma(0°) + at$ where t is in degrees Celsius.

Table 12. Quantum Yields for NO_2 Photolysis

λ, nm	Φ	λ, nm	Φ
< 285	1.000	393	0.953
290	0.999	394	0.950
295	0.998	395	0.942
300	0.997	396	0.922
305	0.996	397	0.870
310	0.995	398	0.820
315	0.994	399	0.760
320	0.993	400	0.695
325	0.992	401	0.635
330	0.991	402	0.560
335	0.990	403	0.485
340	0.989	404	0.425
345	0.988	405	0.350
350	0.987	406	0.290
355	0.986	407	0.225
360	0.984	408	0.185
365	0.983	409	0.153
370	0.981	410	0.130
375	0.979	411	0.110
380	0.975	412	0.094
381	0.974	413	0.083
382	0.973	414	0.070
383	0.972	415	0.059
384	0.971	416	0.048
385	0.969	417	0.039
386	0.967	418	0.030
387	0.966	419	0.023
388	0.964	420	0.018
389	0.962	421	0.012
390	0.960	422	0.008
391	0.959	423	0.004
392	0.957	424	0.000

$$NO_3 + h\nu \rightarrow NO + O_2 \quad (\Phi_1)$$

$$\rightarrow NO_2 + O \quad (\Phi_2)$$

The absorption cross sections of the nitrate free radical, NO_3, have been studied by (1) Johnston and Graham (1974); (2) Graham and Johnston (1978); (3) Mitchell et al (1980); (4) Marinelli et al (1982); (5) Ravishankara and Wine (1983); (6) Cox et al (1984a); (7) Burrows et al (1985b); (8) Ravishankara and Mauldin (1986); (9) Sander (1986); (10) Cantrell et al (1987); and (11) Canosa-Mas et al (1987). The 1st and 4th studies required calculation of the NO_3 concentration by modeling a complex kinetic system. The other studies are more direct and the results in terms of integrated absorption coefficients are in good agreement. The recommended value at 298 K and 662 nm, $(2.00 \pm 0.25) \times 10^{-12}$ cm^2, is the average of the results of studies (4), (5) and (7) through (11). The values in the wavelength range 600-670 nm, shown in Figure 2 and listed in Table 13, were calculated using the spectra measured in studies (8), (9) and (11), and normalizing the 662 nm value to the above average. The spectra obtained in other studies are very similar to the recommended values. The original literature should be consulted for a more extended wavelength range. The temperature dependence of the 662 nm band has been studied by Ravishankara and Mauldin (1986), Sander (1986) and Cantrell et al (1987), while the first two investigators observe the cross section at 662 nm to increase with decreasing temperature, Cantrell et al (1987) found no measurable temperature dependence. The reason for this discrepancy is not clear.

The quantum yields Φ_1 and Φ_2 have been measured by Graham and Johnston (1978), and under higher resolution by Magnotta and Johnston (1980), who report the product of the cross section times the quantum yield in the 400 to 630 nm range. The total quantum yield value, $\Phi_1 + \Phi_2$, computed from the results of this latter study and the cross sections of Graham and Johnston (1978), is above unity for $\lambda < 610$ nm, which is, of course, impossible. Hence, there is some systematic error and it is most likely in the primary quantum yield measurements. Magnotta and Johnston (1980) and Marinelli et al (1982) have discussed the probable sources of this error, but the question remains to be resolved and further studies are in order. At present, the recommendation remains unchanged; namely, to use the following photodissociation rates estimated by Magnotta and Johnston (1980) for overhead sun at the earth's surface:

$$J_1(NO + O_2) = 0.022 \text{ s}^{-1}$$

$$J_2(NO_2 + O) = 0.18 \text{ s}^{-1}.$$

Table 13. Absorption Cross Sections of NO_3 at 298 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
600	258	625	796	648	60
601	263	626	703	649	51
602	302	627	715	650	49
603	351	628	702	651	52
604	413	629	672	652	55
605	415	630	638	653	61
606	322	631	470	654	76
607	225	632	344	655	93
608	170	633	194	656	131
609	153	634	142	657	172
610	192	635	128	658	222
611	171	636	159	659	356
612	202	637	191	660	658
613	241	638	193	661	1308
614	242	639	162	662	2000
615	210	640	121	663	1742
616	190	641	99	664	1110
617	189	642	91	665	752
618	208	643	93	666	463
619	229	644	92	667	254
620	292	645	85	668	163
621	450	646	72	669	113
622	941	647	69	670	85
623	1407				
624	1139				
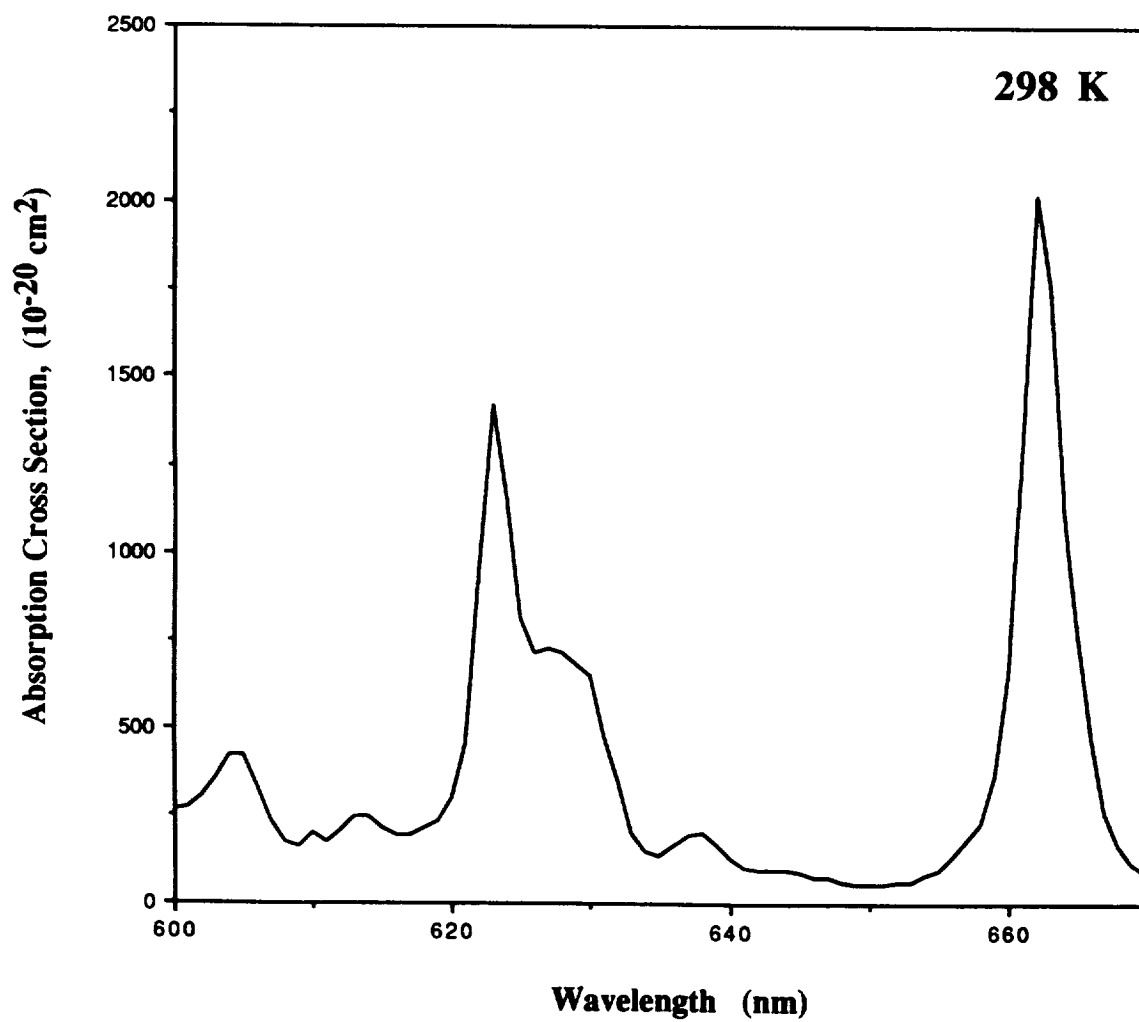
Figure 2. Absorption Spectrum of NO_3

$N_2O + h\nu \rightarrow N_2 + O(^1D)$
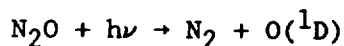
The recommended values are taken from the work of Selwyn et al (1977), who measured the temperature dependence of the absorption cross sections in the atmospherically relevant wavelength region. They have fitted their data with the expression shown in Table 14; Table 15 presents the room temperature data. Hubrich and Stuhl (1980) remeasured the N_2O cross sections at 298 K and 208 K, and their results are in very good agreement with those of Selwyn et al. The quantum yield for photodissociation is unity and the products are N_2 and $O(^1D)$ (Zelikoff and Aschenbrand, 1954; Paraskevopoulos and Cvetanovic, 1969; Preston and Barr, 1971; Simonaitis et al, 1972). The yield of $N(^4s)$ and $NO(^2\Pi)$ is less than 1% (Greenblatt and Ravishankara, 1989).

Table 14. Mathematical Expression for Absorption Cross Sections of N_2O as a Function of Temperature

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$$\ln \sigma(\lambda,T) = \sum_{n=o}^{4} A_n \lambda^n + (T-300) \exp(\sum_{n=o}^{3} B \lambda^n)$$

where T: temperature, Kelvin; λ : nm

$A_0 = 68.21023$	$B_0 = 123.4014$
$A_1 = -4.071805$	$B_1 = -2.116255$
$A_2 = 4.301146 \times 10^{-2}$	$B_2 = 1.111572 \times 10^{-2}$
$A_3 = -1.777846 \times 10^{-4}$	$B_3 = -1.881058 \times 10^{-5}$
$A_4 = 2.520672 \times 10^{-7}$	

Range: 173 to 240 nm; 194 to 320 K

Table 15. Absorption Cross Sections of N_2O at 298 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
173	11.3	196	6.82	219	0.115
174	11.9	197	6.10	220	0.0922
175	12.6	198	5.35	221	0.0739
176	13.4	199	4.70	222	0.0588
177	14.0	200	4.09	223	0.0474
178	13.9	201	3.58	224	0.0375
179	14.4	202	3.09	225	0.0303
180	14.6	203	2.67	226	0.0239
181	14.6	204	2.30	227	0.0190
182	14.7	205	1.95	228	0.0151
183	14.6	206	1.65	229	0.0120
184	14.4	207	1.38	230	0.00955
185	14.3	208	1.16	231	0.00760
186	13.6	209	0.980	232	0.00605
187	13.1	210	0.755	233	0.00478
188	12.5	211	0.619	234	0.00360
189	11.7	212	0.518	235	0.00301
190	11.1	213	0.421	236	0.00240
191	10.4	214	0.342	237	0.00191
192	9.75	215	0.276	238	0.00152
193	8.95	216	0.223	239	0.00123
194	8.11	217	0.179	240	0.00101
195	7.57	218	0.142		
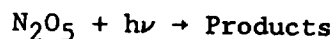
The absorption cross sections of dinitrogen pentoxide, N_2O_5, have been measured at room temperature by Jones and Wulf (1937) between 285 and 380 nm, by Johnston and Graham (1974) between 210 and 290 nm, by Graham (1975) between 205 and 380 nm; and for temperatures in the 223 to 300 K range by Yao et al (1982), between 200 and 380 nm. The agreement is good, particularly considering the difficulties in handling N_2O_5. The recommended cross section values, listed in Table 16, are taken from Yao et al (1982); for wavelengths shorter than 280 nm there is little or no temperature dependence, and between 285 and 380 nm the temperature effect is best computed with the expression listed at the bottom of Table 16.

There are now several studies on the primary photolysis products of N_2O_5: Swanson et al (1984) have measured the quantum yield for NO_3 production at 249 and at 350 nm, obtaining a value close to unity, which is consistent with the observations of Burrows et al (1984b) for photolysis at 254 nm. Barker et al (1985) report a quantum yield for $O(^3P)$ production at 290 nm of less than 0.1, and near unity for NO_3. For O-atom production Margitan (private communication, 1985) measured a quantum yield value of 0.35 at 266 nm, and Ravishankara et al (1986) report values of 0.72, 0.38, 0.21 and 0.15 at 248, 266, 287 and 289 nm, respectively, with a quantum yield near unity for NO_3 production at all these wavelengths. It appears, then, that NO_3 is produced with unit quantum yield while the O-atom and hence the NO yield increases at shorter wavelengths with a consequent decrease in the NO_2 yield. The study of Oh et al (1986) indicates that, besides NO_3, the primary photolysis products are a wavelength dependent mixture of NO_2, NO_2* and NO + O, where NO_2* represents one or more excited electronic states, most likely the $^2B_1$ state.

Table 16. Absorption Cross Sections of N_2O_5

| λ(nm)	$10^{20}\sigma(cm^2)$	λ(nm)	$10^{20}\sigma(cm^2)$
200	920	245	52
205	820	250	40
210	560	255	32
215	370	260	26
220	220	265	20
225	144	270	16.1
230	99	275	13.0
235	77	280	11.7
240	62		

For 285 nm < λ < 380 nm; 300 K > T > 225 K:
$10^{20}\sigma = \exp[2.735 + ((4728.5 - 17.127\lambda)/T)]$
where σ is in cm^2/molecule; λ in nm; and T in Kelvin.

HONO + $h\nu \rightarrow$ HO + NO
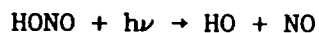
The ultraviolet spectrum of HONO between 300 and 400 nm has been studied by Stockwell and Calvert (1978) by examination of its equilibrium mixtures with NO, NO_2, H_2O, N_2O_3 and N_2O_4; the possible interferences by these compounds were taken into account. The recommended cross sections, taken from this work, are listed in Table 17.

Table 17. HONO Absorption Cross Sections

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
310	0.0	339	16.3	368	45.0
311	0.0	340	10.5	369	29.3
312	0.2	341	8.70	370	11.9
313	0.42	342	33.5	371	9.46
314	0.46	343	20.1	372	8.85
315	0.42	344	10.2	373	7.44
316	0.3	345	8.54	374	4.77
317	0.46	346	8.32	375	2.7
318	3.6	347	8.20	376	1.9
319	6.10	348	7.49	377	1.5
320	2.1	349	7.13	378	1.9
321	4.27	350	6.83	379	5.8
322	4.01	351	17.4	380	7.78
323	3.93	352	11.4	381	11.4
324	4.01	353	37.1	382	14.0
325	4.04	354	49.6	383	17.2
326	3.13	355	24.6	384	19.9
327	4.12	356	11.9	385	19.0
328	7.55	357	9.35	386	11.9
329	6.64	358	7.78	387	5.65
330	7.29	359	7.29	388	3.2
331	8.70	360	6.83	389	1.9
332	13.8	361	6.90	390	1.2
333	5.91	362	7.32	391	0.5
334	5.91	363	9.00	392	0.0
335	6.45	364	12.1	393	0.0
336	5.91	365	13.3	394	0.0
337	4.58	366	21.3	395	0.0
338	19.1	367	35.2	395	0.0

$HNO_3 + h\nu \rightarrow OH + NO_2$
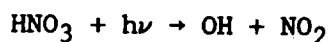
The recommended absorption cross sections, listed in Table 18, are taken from the work of Molina and Molina (1981). These data are in good agreement throughout the 190-330 nm range with the values reported by Biaume (1973). They are also in very good agreement with the data of Johnston and Graham (1973) except towards both ends of the wavelength range. Okabe (1980) has measured the cross sections in the 110-190 nm range; his results are 20-30% lower than those of Biaume and of Johnston and Graham around 185-190 nm.

Johnston et al (1974) measured a quantum yield value of ~1 for the $OH + NO_2$ channel in the 200-315 nm range, using end product analysis. The quantum yield for O-atom production at 266 nm has been measured to be 0.03, and that for H-atom production less than 0.002, by Margitan and Watson (1982), who looked directly for these products using atomic resonance fluorescence. Jolly et al (1986) measured a quantum yield for OH production of 0.89 ± 0.08 at 222 nm. Vaghjiani and Ravishankara (private communication) have measured a quantum yield of unity for OH production at 248 nm. It appears that for atmospheric purposes OH and NO_2 are the only major products.

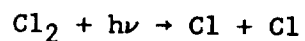Table 18. Absorption Cross Sections of HNO_3 Vapor at 298 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	1560	260	1.88
195	1150	265	1.71
200	661	270	1.59
205	293	275	1.35
210	105	280	1.10
215	35.6	285	0.848
220	15.1	290	0.607
225	8.62	295	0.409
230	5.65	300	0.241
235	3.72	305	0.146
240	2.57	310	0.071
245	2.10	315	0.032
250	1.91	320	0.012
255	1.90	325	0.005
		330	0.002

$HO_2NO_2 + h\nu \rightarrow$ Products
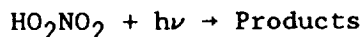
There are five studies of the UV spectrum of HO_2NO_2 vapor: Cox and Patrick (1979), Morel et al (1980), Graham et al (1978b), Molina and Molina (1981), and Singer et al (1989).   The latter three studies are the only ones covering the gas phase spectrum in the critical wavelength range for atmospheric photodissociation, that is, wavelengths longer than 290 nm. The recommended values, listed in Table 19, are an average of the work of Molina and Molina (1981) and of Singer et al (1989), which are the more direct studies.   The cross sections appear to be temperature-independent between 298 and 253 K (Singer et al, 1989).   MacLeod et al (1988) report that photolysis at 248 nm yields one third OH and NO_3 and two thirds $HO_2 + NO_2$.

Table 19.   Absorption Cross Sections of HO_2NO_2 Vapor

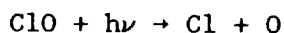| λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	1010	260	28.5
195	816	265	23.0
200	563	270	18.1
205	367	275	13.4
210	239	280	9.3
215	161	285	6.2
220	118	290	3.9
225	93.5	295	2.4
230	79.2	300	1.4
235	68.2	305	0.9
240	58.1	310	0.5
245	48.9	315	0.3
250	41.2	320	0.2
255	35.0	325	0.1

$Cl_2 + h\nu \rightarrow Cl + Cl$

The absorption cross sections of Cl_2, listed in Table 20, are taken from the work of Seery and Britton (1964). These results are in good agreement with those reported by Gibson and Bayliss (1933), Fergusson et al (1936), and Burkholder and Bair (1983).
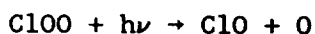
Table 20. Absorption Cross Sections of Cl_2

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
240	0.08	350	18.9
250	0.12	360	13.1
260	0.23	370	8.3
270	0.88	380	4.9
280	2.7	390	3.3
290	6.5	400	1.9
300	12.0	410	1.3
310	18.5	420	0.99
320	23.6	430	0.73
330	25.6	440	0.53
340	23.6	450	0.34

ClO + hν → Cl + O

The absorption cross sections of chlorine monoxide, ClO, have been reviewed by Watson (1977). There are more recent measurements yielding results in reasonable agreement with the earlier ones, (1) by Mandelman and Nicholls (1977) in the 250-310 nm region; (2) by Wine et al (1977) around 283 nm; (3) and by Rigaud et al (1977), (4) Jourdain et al (1978), (5) Sander and Friedl (1989), (6) Simon et al (1989), and (7) Trolier et al (1990) in the 270-310 nm region. The peak cross section at the top of the continuum is 5.2×10^{-18}, based on the average of studies (4), (5), (6), (7) and Johnston et al (1969). Figure 3 shows a spectrum of ClO. It should be noted that the cross sections on the structured part are extremely dependent on instrument resolution, and the figure is only a guide to the line positions and approximate shapes. The cross sections of the continuum are independent of temperature (Trolier et al (1990), while the structured part is extremely temperature dependent. The bands sharpen and grow with a decrease in temperature.

The calculations of Coxon et al (1976) and Langhoff et al (1977) indicate that photodecomposition of ClO accounts for at most 2 to 3 percent of the total destruction rate of ClO in the stratosphere, which occurs predominantly by reaction with oxygen atoms and nitric oxide.

ClOO + hν → ClO + O

Johnston et al (1969) measured the absorption cross sections of the ClOO radical using a molecular modulation technique which required interpretation of a complex kinetic scheme. The values listed in Table 21 are taken from their work.

Table 21. Absorption Cross Sections of ClOO

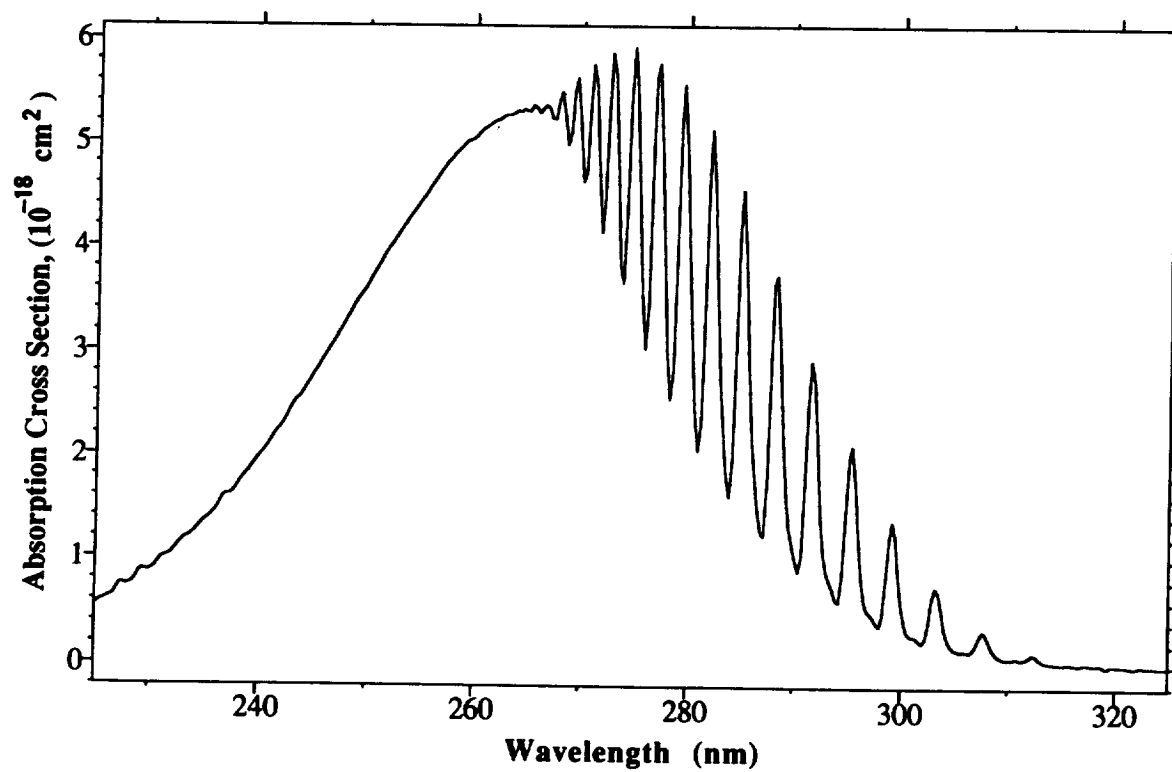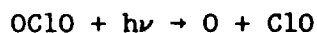| λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
225	260	255	1240
230	490	260	1000
235	780	265	730
240	1050	270	510
245	1270	275	340
250	1230	280	230

Figure 3.   Absorption Spectrum of ClO

OClO + hν → O + ClO

The spectrum of OClO is characterized by a series of well developed progressions of bands extending from ~280 to 480 nm. The spectroscopy of this molecule has been studied extensively, and the quantum yield for photodissociation appears to be unity throughout the above wavelength range. See, for example, the review by Watson (1977). Birks et al (1977) have estimated a half-life against atmospheric photodissociation of OClO of a few seconds.

The recommended absorption cross section values are those reported by Wahner et al (1987), who measured the spectra with a resolution of 0.25 nm at 204, 296 and 378 K, in the wavelength range 240 to 480 nm. Table 22 lists the cross section values at the peak of the bands [a(0) to a(26)]. Figure 4, from Wahner et al, shows the OClO spectrum at 220 K and at room temperature.

Table 22. Absorption Cross Sections of OClO at the Band Peaks

| λ(nm)	$10^{20}\sigma$ (cm^2)		
	204 K	296 K	378 K
475.53	-	13	-
461.15	17	17	16
446.41	94	69	57
432.81	220	166	134
420.58	393	304	250
408.83	578	479	378
397.76	821	670	547
387.37	1046	844	698
377.44	1212	992	808
368.30	1365	1136	920
359.73	1454	1219	984
351.30	1531	1275	989
343.44	1507	1230	938
336.08	1441	1139	864
329.22	1243	974	746
322.78	1009	791	628
317.21	771	618	516
311.53	542	435	390
305.99	393	312	291
300.87	256	219	216
296.42	190	160	167
391.77	138	114	130
287.80	105	86	105
283.51	089	72	90
279.64	073	60	79
275.74	059	46	-
272.93	053	33	-
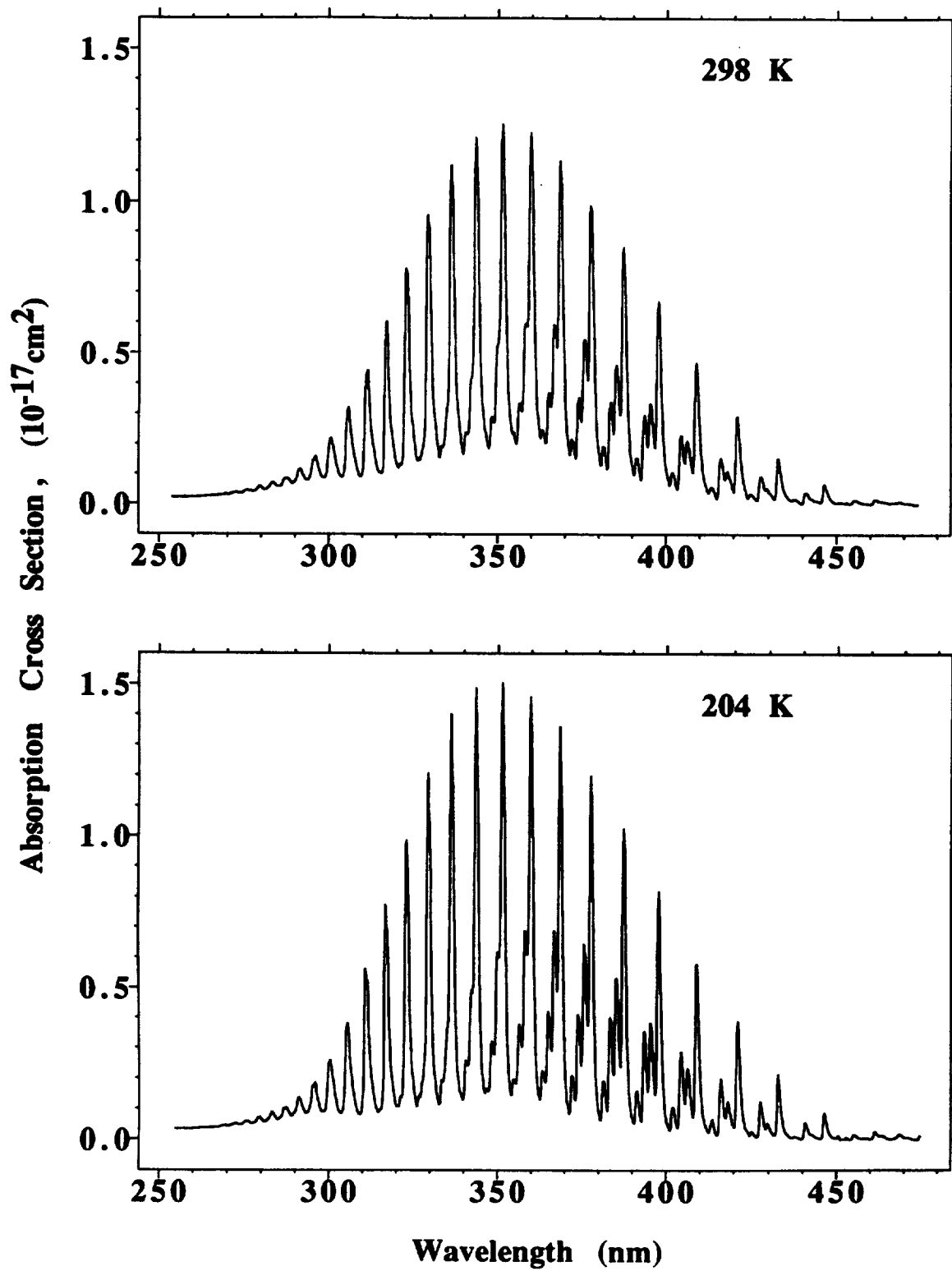
Figure 4. Absorption Spectrum of OClO

$ClO_3 + h\nu \rightarrow$ Products
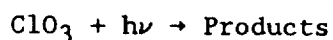
Table 23 lists absorption cross sections of chlorine trioxide, ClO_3, for the 200 to 350 nm range obtained by graphical interpolation between the data points of Goodeve and Richardson (1937). Although the quantum yield for decomposition has not been measured, the continuous nature of the spectrum indicates that it is likely to be unity.

Table 23. ClO_3 Absorption Cross Sections

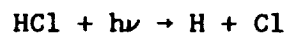| λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
200	530	280	460
210	500	290	430
220	480	300	400
230	430	310	320
240	350	320	250
250	370	330	180
260	430	340	110
270	450	350	76

$Cl_2O_2 + h\nu$
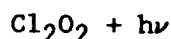
The recommended absorption cross sections for dichlorine peroxide (the ClO dimer), ClOOCl, are listed in Table 24. The values are the smoothed average of the results reported by Cox and Hayman (1988), DeMore and Tschuikow-Roux (1989), Permien et al (1988), and Burkholder et al (1989). These measurements were carried out in the 200-250 K temperature range; thermal decomposition of the dimer occurs very fast at higher temperatures. There is general agreement among these workers on the shape of the spectrum, and the cross section values at the maximum at about 245 nm are within 10%. There are, however, significant discrepancies, i.e., around 280 nm. The results of Burkholder et al (1989) are about 35% larger than those of the other three data sets. More accurate measurements are needed, particularly beyond 290 nm, in order to better estimate atmospheric photodissociation rates. Recent studies have shown that the UV spectrum originally attributed by Molina and Molina (1988) to Cl_2O_2 is actually the spectrum of Cl_2O_3, which is a ClO-OClO adduct (Cox and Hayman, 1988; DeMore and Tschuikow-Roux, 1990; Permien et al, 1988; Burkholder et al, 1990). These studies also indicate that only one stable species is produced in the recombination reaction of ClO with itself, and that this species is dichlorine peroxide, ClOOCl, rather than ClOClO. Using submillimeter wave spectroscopy, Birk et al (1989) have further established the structure of the recombination product

to be ClOOCl. These observations are in agreement with the results of quantum mechanical calculations (McGrath et al, 1988). The quantum yield for photodissociation is believed to be unity, with the products probably being Cl + ClOO (Cox and Hayman, 1988). However, further experimental verification is required.

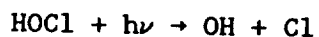Table 24. Absorption Cross Sections of ClOOCl around 200-250 K

λ (nm)	σ $(10^{20}cm^2)$	λ (nm)	σ $(10^{20}cm^2)$	λ (nm)	σ $(10^{20}cm^2)$	λ (nm)	σ $(10^{20}cm^2)$
200	383.5	240	600.3	280	172.5	320	25.6
202	352.9	242	625.7	282	159.6	322	23.4
204	325.3	244	639.4	284	147.3	324	21.4
206	298.6	246	642.6	286	136.1	326	19.2
208	274.6	248	631.5	288	125.2	328	17.8
210	251.3	250	609.3	290	114.6	330	16.7
212	231.7	252	580.1	292	104.6	332	15.6
214	217.0	254	544.5	294	95.4	334	14.4
216	207.6	256	505.4	296	87.1	336	13.3
218	206.1	258	463.1	298	79.0	338	13.1
220	212.1	260	422.0	300	72.2	340	12.1
222	227.1	262	381.4	302	65.8	342	11.5
224	249.4	264	344.6	304	59.9	344	10.9
226	280.2	266	311.6	306	54.1	346	10.1
228	319.5	268	283.3	308	48.6	348	9.0
230	365.0	270	258.4	310	43.3	350	8.2
232	415.4	272	237.3	312	38.5	352	7.9
234	467.5	274	218.3	314	34.6	354	6.8
236	517.5	276	201.6	316	30.7	356	6.1
238	563.0	278	186.4	318	28.0	358	5.8
						360	5.5

$HCl + h\nu \rightarrow H + Cl$

The absorption cross sections of HCl, listed in Table 25, are taken from the work of Inn (1975).

Table 25. Absorption Cross Sections of HCl Vapor

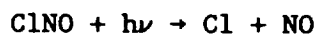| λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
140	211	185	31.3
145	281	190	14.5
150	345	195	6.18
155	382	200	2.56
160	332	205	0.983
165	248	210	0.395
170	163	215	0.137
175	109	220	0.048
180	58.8		

HOCl + hν → OH + Cl

The absorption cross sections of HOCl vapor have been measured by several groups. Molina and Molina (1978) and Knauth et al (1979) produced this species using equilibrium mixtures with Cl_2O and H_2O; their results provided the basis for the earlier recommendation. More recently, Mishalanie et al (1986) and Permien et al (1988) used a dynamic source to generate the HOCl vapor. The cross section values reported by Molina and Molina (1978), Mishalanie et al (1986), and Permien et al (1988) are within 20% between 250 and 330 nm. In this wavelength range, the values reported by Knauth et al (1977) are significantly smaller, e.g., a factor of four at 280 nm. Beyond 340 nm, the cross sections of Mishalanie et al are much smaller than those obtained by the other three groups: at 365 nm, the discrepancy is about an order of magnitude.

The recommended values are taken from the work of Permien et al; they are listed in Table 26. These authors were able to produce HOCl vapor in the absence of significant amounts of other absorbing gases such as Cl_2 and Cl_2O. The corrections due to the presence of these impurities are the most likely source of error in most of the investigations.

Molina et al (1980b) observed production of OH radicals in the laser photolysis of HOCl around 310 nm, and Butler and Phillips (1983) found no evidence for O-atom production at 308 nm, placing an upper limit of ~0.02 for the primary quantum yield for the HCl + O channel.

Table 26. Absorption Cross Sections of HOCl

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
215	8.71	295	16.12
220	13.26	300	14.55
225	18.95	305	12.30
230	25.33	310	10.43
235	31.48	315	8.60
240	36.48	320	6.95
245	38.89	325	5.54
250	40.49	330	4.35
255	38.54	335	3.32
260	34.11	340	2.48
265	28.34	345	1.83
270	23.61	350	1.34
275	20.63	355	0.92
280	19.18	360	0.61
285	18.26	365	0.42
290	17.38	370	0.27
		375	0.15

ClNO + hν → Cl + NO

Nitrosyl chloride has a continuous absorption extending beyond 650 nm. There is good agreement between the work of Martin and Gareis (1956) for the 240 to 420 nm wavelength region, of Ballash and Armstrong (1974) for the 185 to 540 nm region, of Illies and Takacs (1976) for the 190 to 400 nm region, and of Tyndall et al (1987) for the 190 to 350 region except around 230 nm, where the values of Ballash and Armstrong are larger by almost a factor of two. The recommended absorption cross sections, listed in Table 27, are taken from the recent work of Tyndall et al (1987).

The quantum yield for the primary photolytic process has been reviewed by Calvert and Pitts (1966a); it is unity over the entire visible and near-ultraviolet bands.

Table 27. ClNO Absorption Cross Sections

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	4320	230	266	270	12.9	310	11.5
192	5340	232	212	272	12.3	312	11.9
194	6150	234	164	274	11.8	314	12.2
196	6480	236	120	276	11.3	316	12.5
198	6310	238	101	278	10.7	318	13.0
200	5860	240	82.5	280	10.6	320	13.4
202	5250	242	67.2	282	10.2	322	13.6
204	4540	244	55.1	284	9.99	324	14.0
206	3840	246	45.2	286	9.84	326	14.3
208	3210	248	37.7	288	9.71	328	14.6
210	2630	250	31.7	290	9.64	330	14.7
212	2180	252	27.4	292	9.63	332	14.9
214	1760	254	23.7	294	9.69	334	15.1
216	1400	256	21.3	296	9.71	336	15.3
218	1110	258	19.0	298	9.89	338	15.3
220	896	260	17.5	300	10.0	340	15.2
222	707	262	16.5	302	10.3	342	15.3
224	552	264	15.3	304	10.5	344	15.1
226	436	266	14.4	306	10.8	346	15.1
228	339	268	13.6	308	11.1	348	14.9
						350	14.5

$ClNO_2 + h\nu \rightarrow$ Products

The absorption cross sections of nitryl chloride, $ClNO_2$, have been measured between 230 and 330 nm by Martin and Gareis (1956), between 185 and 400 nm by Illies and Takacs (1976), and between 270 and 370 nm by Nelson and Johnston (1981). The results are in good agreement below 300 nm. Table 28 lists the recommended values, which are taken from Illies and Takacs (1976) between 190 and 270 nm, and from Nelson and Johnston (1981) between 270 and 370 nm. These latter authors showed that an approximate 6% Cl_2 impurity in the samples used by Illies and Takacs could explain the discrepancy in the results above 300 nm. Nelson and Johnston (1981) report a value of one (within experimental error) for the quantum yield for production of chlorine atoms; they also report a negligible quantum yield for the production of oxygen atoms.

Table 28. Absorption Cross Sections of $ClNO_2$

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	2690	290	18.1
200	455	300	15.5
210	339	310	12.5
220	342	320	8.70
230	236	330	5.58
240	140	340	3.33
250	98.5	350	1.78
260	63.7	360	1.14
270	37.2	370	0.72
280	22.3		

ClONO + hν → Products

Measurements in the near-ultraviolet of the cross sections of chlorine nitrite (ClONO) have been made by Molina and Molina (1977). Their results are listed in Table 29. The characteristics of the spectrum and the instability of ClONO strongly suggest that the quantum yield for decomposition is unity. The Cl-O bond strength is only about 20 kilocalories, so that chlorine atoms are likely photolysis products.

Table 29. ClONO Absorption Cross Sections at 231 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
235	215.0	320	80.3
240	176.0	325	75.4
245	137.0	330	58.7
250	106.0	335	57.7
255	65.0	340	43.7
260	64.6	345	35.7
265	69.3	350	26.9
270	90.3	355	22.9
275	110.0	360	16.1
280	132.0	365	11.3
285	144.0	370	9.0
290	144.0	375	6.9
295	142.0	380	4.1
300	129.0	385	3.3
305	114.0	390	2.2
310	105.0	395	1.5
315	98.1	400	0.6

$ClONO_2 + h\nu \rightarrow$ Products

The recommended cross section values, listed in Table 30, are taken from the work of Molina and Molina (1979), which supersedes the earlier work of Rowland, Spencer and Molina (1976).

The identity of the primary photolytic fragments has been investigated by several groups. Smith et al (1977) report $O + ClONO$ as the most likely products, using end product analysis and steady-state photolysis. The results of Chang et al (1979b), who employed the "Very Low Pressure Photolysis" (VLPPh) technique, indicate that the products are $Cl + NO_3$. Adler-Golden and Wiesenfeld (1981), using a flash photolysis atomic absorption technique, find O-atoms to be the predominant photolysis product, and report a quantum yield for Cl-atom production of less than 4%. Marinelli and Johnston (1982b) report a quantum yield for NO_3 production at 249 nm between 0.45 and 0.85 with a most likely value of 0.55; they monitored NO_3 by tunable dye-laser absorption at 662 nm. Margitan (1983a) used atomic resonance fluorescence detection of O- and Cl-atoms and found the quantum yield at 266 and at 355 nm to be 0.9 ± 0.1 for Cl-atom production, and ~0.1 for O-atom production, with no discernible difference at the two wavelengths. Burrows et al (1988) report also Cl and NO_3 as the photolysis products at 254 nm, with a quantum yield of unity within experimental error.

The preferred quantum yield values are 0.9 for the $Cl + NO_3$ channel, and a complementary value of 0.1 for the $O + ClONO$ channel. The recommendation is based on Margitan (1983a), whose direct study is the only one with results at a wavelength longer than 290 nm, which is where atmospheric photodissociation will predominantly occur. The reason for the discrepancy with the studies by Adler-Golden and Weisenfeld (1981) and by Marinelli and Johnston (1982b) is almost surely that the rate constant for $Cl + ClNO_3$ is much faster (two orders of magnitude) than previously thought (Margitan, 1983a; Kurylo et al, 1983a).

Table 30. Absorption Cross Sections of $ClONO_2$

λ (nm)	$10^{20}\sigma(cm^2)$ 227K	243K	296K	λ (nm)	$10^{20}\sigma(cm^2)$ 227K	243K	296K
190	555	-	589	325	0.463	0.502	0.655
195	358	-	381	330	0.353	0.381	0.514
200	293	-	307	335	0.283	0.307	0.397
205	293	-	299	340	0.246	0.255	0.323
210	330	-	329	345	0.214	0.223	0.285
215	362	-	360	350	0.198	0.205	0.246
220	348	-	344	355	0.182	0.183	0.218
225	282	-	286	360	0.170	0.173	0.208
230	206	-	210	365	0.155	0.159	0.178
235	141	-	149	370	0.142	0.140	0.162
240	98.5	-	106	375	0.128	0.130	0.139
245	70.6	-	77.0	380	0.113	0.114	0.122
250	52.6	50.9	57.7	385	0.098	0.100	0.108
255	39.8	39.1	44.7	390	0.090	0.083	0.090
260	30.7	30.1	34.6	395	0.069	0.070	0.077
265	23.3	23.1	26.9	400	0.056	0.058	0.064
270	18.3	18.0	21.5	405	-	-	0.055
275	13.9	13.5	16.1	410	-	-	0.044
280	10.4	9.98	11.9	415	-	-	0.035
285	7.50	7.33	8.80	420	-	-	0.027
290	5.45	5.36	6.36	425	-	-	0.020
295	3.74	3.83	4.56	430	-	-	0.016
300	2.51	2.61	3.30	435	-	-	0.013
305	1.80	1.89	2.38	440	-	-	0.009
310	1.28	1.35	1.69	445	-	-	0.007
315	0.892	0.954	1.23	450	-	-	0.005
320	0.630	0.681	0.895				

Halocarbon Absorption Cross Sections and Quantum Yields

The primary process in the photodissociation of chlorinated hydrocarbons is well established: absorption of ultraviolet radiation in the lowest frequency band is interpreted as an $n-\sigma^*$ transition involving excitation to a repulsive electronic state (antibonding in C-Cl), which dissociates by breaking the carbon chlorine bond (Majer and Simons, 1964). As expected, the chlorofluoromethanes, which are a particular type of chlorinated hydrocarbons, behave in this fashion (Sandorfy, 1976). Hence, the quantum yield for photodissociation is expected to be unity for these compounds. There are several studies which show specifically that this is the case for CF_2Cl_2, $CFCl_3$ and CCl_4. These studies, which have been reviewed in CODATA (1982), also indicate that at shorter wavelengths two halogen atoms can be released simultaneously in the primary process.

$CCl_4 + h\nu \rightarrow$ Products; $CCl_3F + h\nu \rightarrow$ Products; $CCl_2F_2 + h\nu \rightarrow$ Products
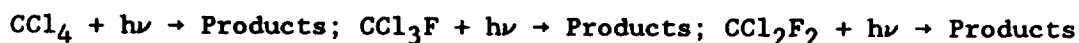
Several authors have reinvestigated the absorption cross sections for CCl_4, CCl_3F, and CCl_2F_2. These include Hubrich et al (1977), Hubrich and Stuhl (1980), Vanlaethem-Meuree et al (1978a,b), and Green and Wayne 1976, 1977). The results are, in general, in very good agreement with our earlier recommendations. Tables 31, 32 and 33 list the present recommendations for the cross sections of CCl_4, CCl_3F and CCl_2F_2, respectively. These data are given by the mean of the values reported by various groups, i.e., those cited above as well as those referred to in earlier evaluations (CODATA, 1982). Absorption cross sections for these species over the temperature range 295-210 K have recently been reported by Simon et al (1988a). These results are in generally good agreement with the present recommendations. For atmospheric photodissociation calculations the change in the cross section values with temperature is negligible for CCl_4 and $CFCl_3$; for CF_2Cl_2 the temperature dependence is given by the expression at the bottom of Table 33.

Table 31. Absorption Cross Sections of CCl_4

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
174	995	218	21.8
176	1007	220	17.0
178	976	222	13.0
180	772	224	9.61
182	589	226	7.19
184	450	228	5.49
186	318	230	4.07
188	218	232	3.01
190	144	234	2.16
192	98.9	236	1.51
194	74.4	238	1.13
196	68.2	240	0.784
198	66.0	242	0.579
200	64.8	244	0.414
202	62.2	246	0.314
204	60.4	248	0.240
206	56.5	250	0.183
208	52.0	255	0.0661
210	46.6	260	0.0253
212	39.7	265	0.0126
214	33.3	270	0.0061
216	27.2	275	0.0024

Table 32. Absorption Cross Sections of CCl_3F

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
170	316	208	21.2
172	319	210	15.4
174	315	212	10.9
176	311	214	7.52
178	304	216	5.28
180	308	218	3.56
182	285	220	2.42
184	260	222	1.60
186	233	224	1.10
188	208	226	0.80
190	178	228	0.55
192	149	230	0.35
194	123	235	0.126
196	99	240	0.0464
198	80.1	245	0.0173
200	64.7	250	0.00661
202	50.8	255	0.00337
204	38.8	260	0.00147
206	29.3		

Table 33. Absorption Cross Sections of CCl_2F_2

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
170	124	200	8.84
172	151	202	5.60
174	171	204	3.47
176	183	206	2.16
178	189	208	1.52
180	173	210	0.80
182	157	212	0.48
184	137	214	0.29
186	104	216	0.18
188	84.1	218	0.12
190	62.8	220	0.068
192	44.5	225	0.022
194	30.6	230	0.0055
196	20.8	235	0.0016
198	13.2	240	0.00029

$$\sigma_T = \sigma_{298}\exp[4.1 \times 10^{-4}(\lambda-184.9)(T-298)]$$

Where: σ_{298} : cross section at 298 K

λ : nm

T   : temperature, Kelvin

$CHClF_2 + h\nu \rightarrow$ Products

The absorption cross sections of $CHClF_2$ (CFC-22) have been measured at room temperature by Robbins and Stolarski (1976) and by Chou et al (1976), at 208 K and 218 K by Hubrich et al (1977), and between 210 and 295 K by Simon et al (1988a). The agreement between these groups is reasonable. The preferred absorption cross sections, listed in Table 34, are taken from the recent work of Simon et al.

Photolysis of $CHClF_2$ is rather unimportant throughout the atmosphere: reaction with OH radicals is the dominant destruction process.

Table 34. Absorption Cross Sections of $CHClF_2$

$\lambda(nm)$	$10^{20}\sigma(cm^2)$				
	295K	270K	250K	230K	210K
174	5.72	5.72	5.72	5.72	5.72
176	4.04	4.04	4.04	4.04	4.04
178	2.76	2.76	2.76	2.76	2.76
180	1.91	1.91	1.91	1.91	1.91
182	1.28	1.28	1.28	1.28	1.28
184	0.842	0.842	0.842	0.842	0.842
186	0.576	0.576	0.576	0.576	0.576
188	0.372	0.372	0.372	0.372	0.372
190	0.245	0.245	0.245	0.245	0.242
192	0.156	0.156	0.156	0.152	0.148
194	0.103	0.102	0.099	0.096	0.093
196	0.072	0.069	0.067	0.064	0.062
298	0.048	0.045	0.043	0.041	0.039
200	0.032	0.029	0.029	0.0259	0.0246
202	0.0220	0.0192	0.0184	0.0169	0.0159
204	0.0142	0.0121	0.0114	0.0104	0.0096

$CH_3Cl + h\nu \rightarrow$ Products
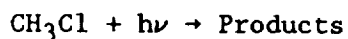
The preferred absorption cross sections, listed in Table 35, are those given by Vanlaethem-Meuree et al (1978b). These values are in very good agreement with those reported by Robbins (1976) at 298 K, as well as with those given by Hubrich et al (1977) at 298 K and 208 K, if the temperature trend is taken into consideration. The results recently reported by Simon et al (1988a) over the temperature range 295-210 K are in excellent agreement with the present recommendation.

Table 35. Absorption Cross Sections of CH_3Cl

λ (nm)	$10^{20}\sigma(cm^2)$		
	296 K	279 K	255 K
186	24.7	24.7	24.7
188	17.5	17.5	17.5
190	12.7	12.7	12.7
192	8.86	8.86	8.86
194	6.03	6.03	6.03
196	4.01	4.01	4.01
198	2.66	2.66	2.66
200	1.76	1.76	1.76
202	1.09	1.09	1.09
204	0.691	0.691	0.691
206	0.483	0.475	0.469
208	0.321	0.301	0.286
210	0.206	0.189	0.172
212	0.132	0.121	0.102
214	0.088	0.074	0.059
216	0.060	0.048	0.033

$CH_3CF_2Cl + h\nu \rightarrow$ Products

The preferred absorption cross sections at 298 K, listed in Table 36 and shown in Figure 5, are the mean of the values reported by Gillotay et al (1989a) and Orlando et al (1990) over the wavelength range where the agreement is better than a factor of two. At lower wavelengths the agreement is much better; e.g., at 200 nm the agreement is within 5%. Green and Wayne (1976/77) and Hubrich and Stuhl (1980) have also measured the cross sections in the ranges 185-200 nm and 160-230 nm, respectively. The results of Green and Wayne are very different from the recommended value and were not considered for this evaluation. The results of Hubrich and Stuhl (reported at 5 nm intervals) are in reasonable agreement with the more recent studies of Gillotay et al and Orlando et al. The temperature dependence of the cross sections has been measured by Orlando et al but has not been included in this evaluation.

$CF_3CHCl_2 + h\nu \rightarrow$ Products

The preferred absorption cross sections at 298 K, listed in Table 36 and shown in Figure 5, are the mean of the values reported by Gillotay et al (1989a) and Orlando et al (1990). The agreement is quite good over the entire wavelength range. The measurements by Green and Wayne (1976/77) over the range 185-205 nm are in reasonable agreement with the recommended value. The temperature dependence of the cross sections has been measured by Orlando et al but is not included here.

$CF_3CHFCl + h\nu \rightarrow$ Products

The preferred value is that reported by Orlando et al (1990), this being the only available set of measurements between 190 and 230 nm. The data are listed in Table 36 and shown in Figure 5. The measurements by Hubrich and Stuhl between 160 and 185 nm do not overlap the range covered by Orlando et al; however, extrapolation (assuming an exponential fall in cross section with wavelength) of Hubrich and Stuhl's results yields values which tend to be higher than those of Orlando. The temperature dependence of the cross section has been measured by Orlando et al but has not been evaluated here. The quantum yield for the dissociation to give Cl atoms is expected to be unity.

$CH_3CFCl_2 + h\nu \rightarrow$ Products

The preferred value, listed in Table 36 and shown in Figure 5, is that reported by Gillotay et al (1989a), which are the only available data. The temperature dependence of the cross sections has not been measured but is expected to be similar to that in CF_3CH_2Cl, CF_3CHCl_2, and CH_3CF_2Cl; i.e., decreasing cross sections with decreasing temperature at longer wavelengths. The quantum yield for dissociation is expected to be unity.

Table 36. Absorption Cross Sections of Hydrochlorofluoroethanes at 298 K

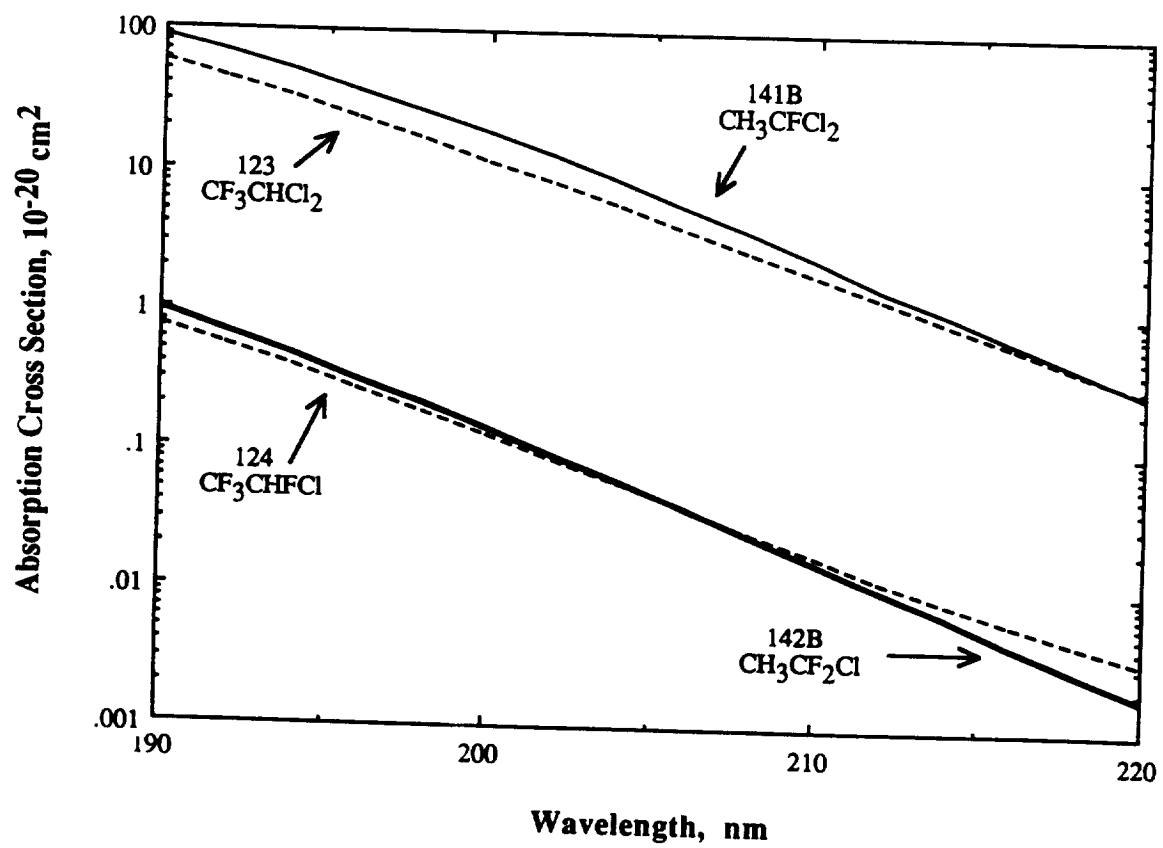| λ (nm)	$10^{20} \sigma$ (cm^2) at 298 K			
	CH_3CFCl_2	CH_3CF_2Cl	CF_3CHCl_2	CF_3CHFCl
190	86.3	0.94	56.7	0.73
192	67.1	0.66	43.2	0.53
194	49.9	0.46	31.7	0.38
196	36.6	0.31	23.0	0.26
198	25.7	0.21	16.4	0.18
200	18.3	0.14	11.5	0.13
202	12.6	0.09	8.1	0.086
204	8.5	0.061	5.6	0.059
206	5.6	0.039	3.0	0.040
208	3.7	0.026	2.7	0.026
210	2.4	0.017	1.8	0.018
212	1.5	0.010	1.3	0.012
214	0.98	0.007	0.85	0.008
216	0.63	0.004	0.58	0.006
218	0.41	0.003	0.39	0.004
220	0.27	0.002	0.28	0.003

Figure 5. Absorption Spectra of Some Hydrochlorofluoroethanes

$CH_3CCl_3 + h\nu \rightarrow$ Products

The absorption cross sections have been measured by Robbins (1977), by Vanlaethem-Meuree et al (1979) and by Hubrich and Stuhl (1980). These latter authors corrected the results to account for the presence of a UV-absorbing stabilizer in their samples, a correction which might account for the rather large discrepancy with the other measurements. The results of Robbins (1977) and of Vanlaethem-Meuree et al (1979) are in good agreement. The recommended values are taken from this latter work (which reports values at 210 K, 230 K, 250 K, 270 K and 295 K, every 2 nm, and in a separate table at wavelengths corresponding to the wavenumber intervals generally used in stratospheric photodissociation calculations). Table 37 lists the values at 210 K, 250 K and 295 K, every 5 nm; the odd wavelength values were computed by linear interpolation.

Table 37. Absorption Cross Sections of CH_3CCl_3

λ (nm)	$10^{20}\sigma(cm^2)$		
	295 K	250 K	210 K
185	265	265	265
190	192	192	129
200	81.0	81.0	81.0
205	46.0	44.0	42.3
210	24.0	21.6	19.8
215	10.3	8.67	7.47
220	4.15	3.42	2.90
225	1.76	1.28	0.97
230	0.700	0.470	0.330
235	0.282	0.152	0.088
240	0.102	0.048	0.024

$CF_3Br + h\nu \rightarrow$ Products

The preferred absorption cross sections at 298 K, listed in Table 38 and shown in Figure 6, are the mean of the values reported by Gillotay and Simon (1989) at 2 nm intervals and Orlando (private communication, 1989) at 1 nm intervals over the wavelength range where the agreement is acceptable, i.e, better than 70%. At longer wavelengths Orlando et al measure larger values than those reported by Gillotay and Simon. Molina et al (1982) have also measured these cross sections which agree better with Gillotay and Simon. However, the agreement in the wavelength range 190-230 nm among the three studies is excellent. The temperature dependence of the cross sections has been measured by Gillotay and Simon as well as Orlando. The agreement between these two studies is poor. We have not evaluated the temperature dependence of the cross section and the readers are referred to

the investigators for the information. For all the bromofluoromethanes, photolysis is expected to cleave the C-Br band with unit quantum efficiency.

CF_2Br_2 + hν → Products

The preferred absorption cross sections at 298 K, listed in Table 38 and shown in Figure 6, are the mean of the values reported by Gillotay and Simon (1989) at 2 nm intervals and Orlando (private communication, 1989) at 1 nm intervals over the wavelength range where the disagreement is no more than a factor of two. At wavelengths longer than ~250 nm, Orlando measured cross sections larger than those reported by Gillotay and Simon (1989) and Molina et al (1982). The discrepancy increases with wavelength and is more than a factor of two beyond 280 nm. However, the agreement between all three measurements is acceptable below 250 nm. Molina et al's values agree with those of Gillotay and Simon over the entire range of wavelengths. The temperature dependence of the cross sections has been measured by Gillotay and Simon as well as Orlando. The agreement between these two studies is poor.

The quantum yield for the dissociation of CF_2Br_2 is expected to be unity. However, Walton (1972) reports that the quantum yield at 265 nm decreases from unity when the system pressure is raised to 50 torr of CO_2. This uncertainty regarding non-unit quantum yield for the dissociation of CF_2Br_2 needs to be resolved.

CF_2BrCl + hν → Products

The recommended cross sections at 298 K, listed in Table 38 and shown in Figure 6, are the mean of the values reported by Gillotay and Simon (1989) at 2 nm intervals and Orlando (private communication, 1989) at 1 nm intervals. Molina et al (1982) and Giolando et al (1980) have also measured the cross sections at 5 nm and 10 nm intervals, respectively. The agreement between the four studies is quite good.

The temperature dependence of the cross sections has been measured by Gillotay and Simon as well as Orlando. The agreement between the two studies is poor. We have not evaluated the temperature dependence of the cross section and the readers are referred to the investigators for this information.

CF_2BrCF_2Br + hν → Products

The preferred absorption cross sections at 298 K, listed in Table 38 and shown in Figure 6, are the mean of the values reported by Gillotay et al (1988) at 2 nm intervals and Orlando (private communication, 1989) at 1 nm intervals over the wavelength range where the agreement is acceptable, i.e., ~70%. At longer wavelengths, Orlando measured larger cross sections than those measured by Gillotay et al. Molina et al (1982) have also measured these cross sections and they agree with the results of Gillotay et al at longer wavelengths. The agreement between the three studies at wavelengths

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shorter than 250 nm is good. The results of Robbins (1977) are in good agreement with the recommended values.

The temperature dependence of the cross sections has been measured by Gillotay et al (1988) and Orlando. The agreement between the two studies is poor at longer wavelengths. We have not evaluated the temperature dependence of the cross section and the readers are referred to the investigators for the information.

Table 38. Absorption Cross Sections of CF_2ClBr, CF_2Br_2, CF_3Br, and CF_2BrCF_2Br at 298 K

λ (nm)	$10^{20} \sigma$ (cm^2)			
	CF_2ClBr	CF_2Br_2	CF_3Br	CF_2BrCF_2Br
190	47	114	6.5	109
192	58	109	7.5	114
194	70	100	8.6	119
196	83	91	10	122
198	96	82	11	124
200	112	75	11	124
202	118	72	12	124
204	121	74	12	120
206	122	81	13	117
208	121	93	13	112
210	117	110	12	106
212	112	136	12	100
214	106	155	11	92
216	98	180	10	85
218	90	203	8.9	77
220	81	224	7.8	69
222	72	242	6.7	61
224	64	251	5.7	54
226	56	253	4.8	47
228	49	250	3.9	40
230	42	241	3.2	35
232	36	227	2.5	29
234	31	209	1.9	24
236	26	189	1.5	20
238	22	168	1.1	16
240	18	147	0.85	13
242	15	126	0.63	11
244	12	106	0.46	8.4
246	9.9	88	0.34	6.7
248	7.9	73	0.25	5.2

Table 38 Con't.   Absorption Cross Sections of CF_2ClBr, CF_2Br_2, CF_3Br, and CF_2BrCF_2Br at 298 K

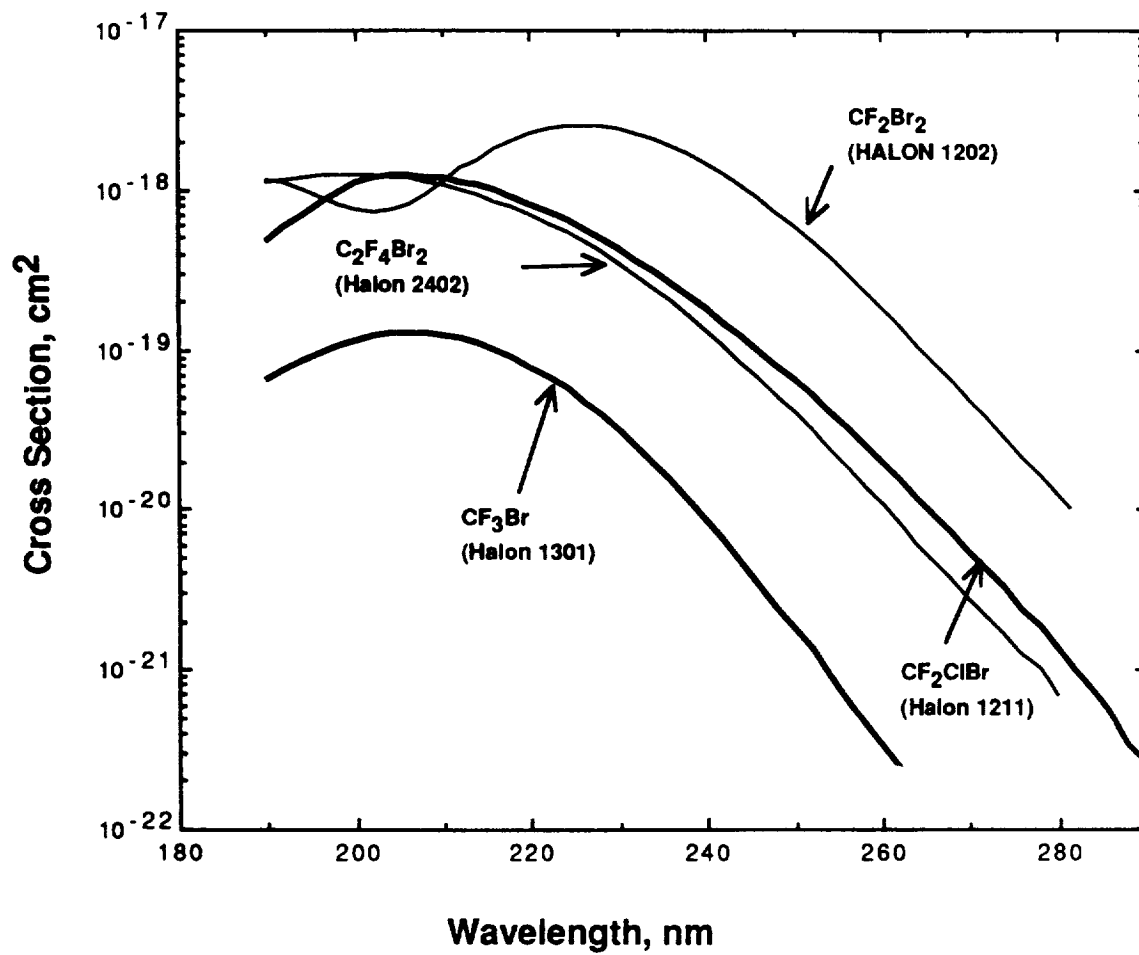| λ (nm)	$10^{20} \ \sigma \ (cm^2)$			
	CF_2ClBr	CF_2Br_2	CF_3Br	CF_2BrCF_2Br
250	6.4	59	0.18	4.1
252	5.2	48	0.13	3.1
254	4.0	38	0.091	2.4
256	3.2	30	0.064	1.9
258	2.5	24	0.046	1.4
260	2.0	18	0.034	1.1
262	1.5	14		0.82
264	1.2	11		0.60
266	0.93	8.4		0.47
268	0.72	6.4		0.36
270	0.54	4.8		0.27
272	0.42	3.7		0.21
274	0.32	2.8		0.16
276	0.24	2.1		0.13
278	0.18	1.6		0.10
280	0.14	1.2		0.068
284	0.072			
286	0.053			
288	0.033			

Figure 6. Absorption Spectra of Some Bromine Compounds

The absorption cross sections for various other halocarbons not listed in this evaluation have also been investigated: for $CClF_3$, CCl_2FCClF_2, $CClF_2CClF_2$ and $CClF_2CF_3$ the values given by Hubrich and Stuhl (1980) at 298 K are in very good agreement with the earlier results of Chou et al (1978) and of Robbins (1977); Hubrich and Stuhl also report values of 208 K for these species. Other absorption cross section measurements include the following: $CHCl_2F$ by Hubrich et al (1977); $CHCl_3$, CH_2Cl_2, CH_2ClF, CF_3CH_2Cl and CH_3CH_2Cl by Hubrich and Stuhl (1980); $CHCl_3$, CH_3Br, $CHFCl_2$, C_2HCl_3 and $C_2H_3Cl_3$ by Robbins (1977); CH_2Cl_2 and $CHCl_3$ by Vanlaethem-Meuree et al (1978a); $CHCl_2F$, $CClF_2CH_2Cl$ and CF_3CH_2Cl by Green and Wayne (1976-1977); and CH_3Br, CH_2Br_2 and $CBrF_2CF_3$ by Molina et al (1982). Simon and co-workers have recently reported absorption cross section measurements over the temperature range 295-210 K for various other halocarbons not listed here. These include the following: $CHCl_3$, CH_2Cl_2, $CHFCl_2$ and CF_3Cl by Simon et al (1988a); CF_3CF_2Cl, CF_2ClCF_2Cl and $CF_2ClCFCl_2$ by Simon et al (1988b); CH_3Br by Gillotary and Simon (1988); and $CHBr_3$ by Gillotay et al (1989b).

As before, the recommendation for the photodissociation quantum yield value is unity for all these species.

CF_4 and C_2F_6 do not have any absorptions at wavelengths longer than 105 and 120 nm, respectively (Sauvageau et al, 1973, 1974; Inn, 1980); therefore, they are not expected to photodissociate until they reach the mesosphere. SF_6 does not absorb at wavelengths longer than 110 nm.

$CCl_2O + h\nu \rightarrow$ Products, $CClFO + h\nu \rightarrow$ Products, and $CF_2O + h\nu \rightarrow$ Products

Table 39 shows the absorption cross sections of CCl_2O (phosgene) and CFClO given by Chou et al (1977), and of CF_2O taken from the work of Molina and Molina (1982). The spectrum of CF_2O shows considerable structure; the values listed in Table 39 are averages over each 50 wavenumber interval. The spectrum of CFClO shows less structure, and the CCl_2O spectrum is a continuum; its photodissociation quantum yield is unity (Calvert and Pitts, 1966a).

The quantum yield for the photodissociation of CF_2O at 206 nm appears to be ~0.25 (Molina and Molina, 1982); additional studies of the quantum yield in the 200 nm region are required in order to establish the atmospheric photodissociation rate.

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Table 39. Absorption Cross Sections of CCl_2O, $CClFO$, and CF_2O

λ (nm)	$10^{20}\sigma(cm^2)$		
	CCl_2O	$CClFO$	CF_2O
184.9	204.0	-	-
186.0	189.0	15.6	5.5
187.8	137.0	14.0	4.8
189.6	117.0	13.4	4.2
191.4	93.7	12.9	3.7
193.2	69.7	12.7	3.1
195.1	52.5	12.5	2.6
197.0	41.0	12.4	2.1
199.0	31.8	12.3	1.6
201.0	25.0	12.0	1.3
103.0	20.4	11.7	0.95
205.1	16.9	11.2	0.69
207.3	15.1	10.5	0.50
209.4	13.4	9.7	0.34
211.6	12.2	9.0	0.23
213.9	11.7	7.9	0.15
216.2	11.6	6.9	0.10
218.6	11.9	5.8	0.06
221.0	12.3	4.8	0.04
223.5	12.8	4.0	0.03
226.0	13.2	3.1	-

BrO + hν → Br + O
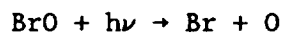
The BrO radical has a banded spectrum in the 290-380 nm range. The strongest absorption feature is around 338 nm. The measured cross sections are both temperature and resolution dependent. As an example, the spectrum measured by Wahner et al (1988) is shown in Figure 7. The bands are due to a vibrational progression in the A ← X system, and the location of the bands, along with the assignments and cross sections measured using 0.4 nm resolution, are shown in Table 40. BrO is expected to dissociate upon light absorption. As a guide, the cross sections averaged over 5 nm wavelength intervals are taken from the work of Cox et al (1982), and are listed in Table 41. These authors estimate a BrO lifetime against atmospheric photodissociation of ~20 seconds at the earth's surface, for a solar zenith angle of 30°.

The earlier BrO cross section measurements were carried out mostly around 338 nm, and have been reviewed by CODATA (1980; 1982).

Table 40. Absorption Cross Sections at the Peak of Various bands in the A ← X Spectrum of BrO

ν',ν''	λ (nm)	$10^{20}\sigma$ (cm^2)	
		298K	223K
13,0	313.5	712	938
12,0	317.0	1010	1360
11,0	320.8	1180	1570
10,0	325.0	1130	1430
9,0	329.1	1130	1390
8,0	333.5	1210	1470
7,0	338.3	1550	1950
6,0	343.7	935	1110
5,0	348.8	703	896
4,0	354.7	722	1050
3,0	360.4	264	344
2,0	367.7	145	154
1,0	374.5	90	96

Spectral resolution is 0.4 nn, fwhm.

Table 41. Absorption Cross Sections of BrO

λ (nm)	$10^{20}\sigma(\text{cm}^2)$ average
300 - 305	200
305 - 310	259
310 - 315	454
315 - 320	391
320 - 325	600
325 - 330	753
330 - 335	628
335 - 340	589
340 - 345	515
345 - 350	399
350 - 355	228
355 - 360	172
360 - 365	161
365 - 370	92
370 - 375	51
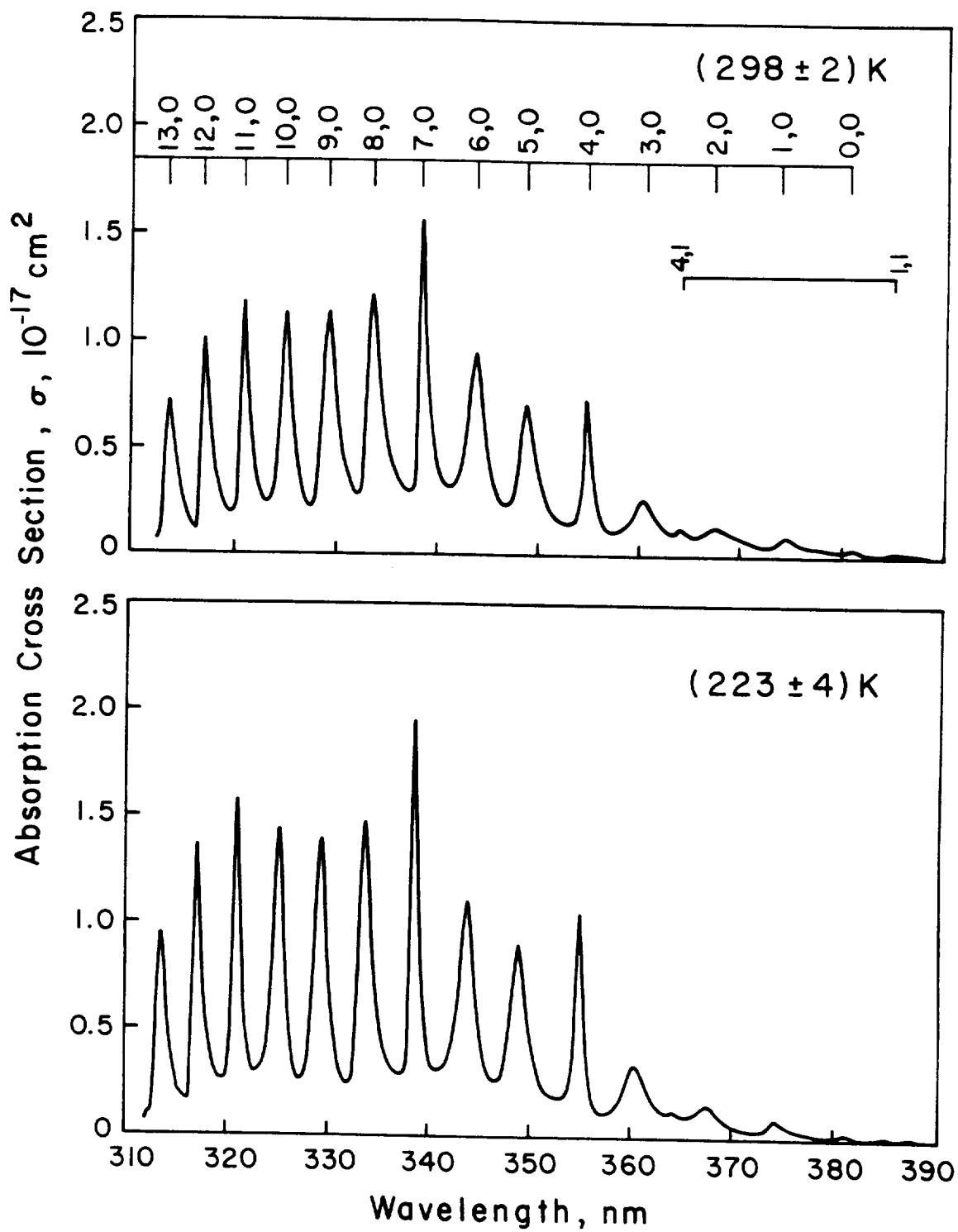
Figure 7.   Absorption Spectrum of BrO

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$BrONO_2 + h\nu \rightarrow$ Products
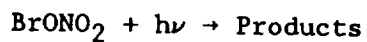
The bromine nitrate cross sections have been measured at room temperature by Spencer and Rowland (1978) in the wavelength region 186-390 nm; their results are given in Table 42. The photolysis products are not known.

Table 42. Absorption Cross Sections of $BrONO_2$

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
186	1500	280	29
190	1300	285	27
195	1000	290	24
200	720	295	22
205	430	300	19
210	320	305	18
215	270	310	15
220	240	315	14
225	210	320	12
230	190	325	11
235	170	330	10
240	130	335	9.5
245	100	340	8.7
250	78	345	8.5
255	61	350	7.7
260	48	360	6.2
265	39	370	4.9
270	34	380	4.0
275	31	390	2.9

$$HF + h\nu \rightarrow H + F$$
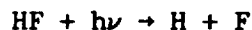
The ultraviolet absorption spectrum of HF has been studied by Safary et al (1951). The onset of absorption occurs at $\lambda < 170$ nm, so that photo-dissociation of HF should be unimportant in the stratosphere.

$$H_2CO + h\nu \rightarrow H + HCO \quad (\Phi_1)$$

$$\rightarrow H_2 + CO \quad (\Phi_2)$$
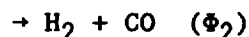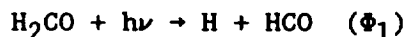
Bass et al (1980) have measured the absorption cross sections of formaldehyde with a resolution of 0.05 nm at 296 K and 223 K. The cross sections have also been measured by Moortgat et al (1980; 1983) with a resolution of 0.5 nm in the 210-360 K temperature range; their values are ~30% larger than those of Bass et al for wavelengths longer than 300 nm. The recommended cross section values, listed in Table 39, are the mean of the two sets of data (as computed in CODATA, 1982).

The quantum yields have been reported with good agreement by Horowitz and Calvert (1978), Clark et al (1978a), Tang et al (1979), Moortgat and Warneck (1979), and Moortgat et al (1980; 1983). The recommended values listed in Table 43 are based on the results of all of these investigators. The quantum yield Φ_2 is pressure dependent for wavelengths longer than 329 nm, and is given by the expression at the bottom of Table 43, which is based on the values reported by Moortgat et al (1980; 1983) for 300 K.

Additional work is needed to determine Φ_1 and the cross sections around 330 nm, which is the important wavelength region for atmospheric photodissociation of CH_2O to yield H + HCO; only a few scattered measurements of Φ_1 have been carried out around this wavelength. At present the recommendation for the 320-340 nm wavelength interval is to calculate Φ_1 by linear interpolation assuming a value of $\Phi_1 = 0.62$ at 320 nm and $\Phi_1 = 0$ at 340 nm.

Table 43. Absorption Cross Sections and Quantum Yields for Photolysis of CH_2O.

λ (nm)	$10^{20}\sigma(cm^2)$		Φ_1 (H + HCO)	Φ_2 (H_2 + CO)
	290 K	220 K		
240	0.03	0.08	0.21	0.42
250	0.13	0.08	0.24	0.46
260	0.47	0.47	0.30	0.48
270	0.86	0.85	0.40	0.46
280	1.86	1.93	0.59	0.35
290	2.51	2.47	0.71	0.26
300	2.62	2.58	0.78	0.22
310	2.45	2.40	0.77	0.23
320	1.85	1.71	0.62	0.38
330	1.76	1.54	0.31	0.69
340	1.18	1.10	0	0.69*
350	0.42	0.39	0	0.40*
360	0.06	0.02	0	0.12*

Note: The values are averaged for 10 nm intervals centered on the indicated wavelength.

* : at P = 760 torr

For λ > 329 nm, Φ_2 at a given wavelength (not averaged over 10 nm intervals) is given by the following expression:

$$\phi_2 = \frac{1 - \exp(112.8 - 0.347\lambda)}{1 + \frac{P}{760}(\frac{\lambda - 329}{364 - \lambda})}$$

λ : nm

P : torr

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$CH_3OOH + h\nu \rightarrow$ Products

Vaghjiani and Ravishankara (1989) have measured the cross sections of CH_3OOH by measuring the CH_3OOH concentration via trapping and titration. These results are recommended and are listed in Table 44. The earlier results of Molina and Arguello (1979) are consistently 40% higher than the values shown in Table 44; this difference is believed to be due to difficulty in trapping CH_3OOH and measuring its concentration. CH_3OOH dissociates upon light absorption to give CH_3O with unit quantum yield (Vaghjiani and Ravishankara, private communication). At shorter wavelength (i.e. 193 nm) production of H and O atoms is also seen.

Table 44. Absorption Cross Sections of CH_3OOH

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
210	31.2	290	0.69
220	15.4	300	0.41
230	9.62	310	0.24
240	6.05	320	0.14
250	3.98	330	0.079
260	2.56	340	0.047
270	1.70	350	0.027
280	1.09	360	0.016

$HCN + h\nu \rightarrow$ Products

Herzberg and Innes (1957) have studied the spectroscopy of hydrogen cyanide, HCN, which starts absorbing weakly at $\lambda < 190$ nm.

The solar photodissociation rate for this molecule is rather small, even in the upper stratosphere; estimates of this rate would require additional studies of the absorption cross sections and quantum yields in the 200 nm region.

$CH_3CN + h\nu \rightarrow$ Products

McElcheran et al (1958) have reported the spectrum of acetonitrile or methyl cyanide, CH_3CN; the first absorption band appears at $\lambda < 220$ nm. More recently, Suto and Lee (1985) and Zetzsch (1989) have measured the cross sections around 200 nm; solar photodissociation is unimportant compared to reaction with OH radicals.

SO_2 + hν → Products
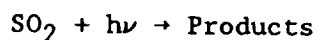
The UV absorption spectrum of SO_2 is highly structured, with a very weak absorption in the 340-390 nm region, a weak absorption in the 260-340 nm, and a strong absorption extending from 180 to 235 nm; the threshold wavelength for photodissociation is ~220 nm. The atmospheric photochemistry of SO_2 has been reviewed by Heicklen et al (1980) and by Calvert and Stockwell (1983). Direct photo-oxidation at wavelengths longer than ~300 nm by way of the electronically excited states of SO_2 appears to be relatively unimportant.

The absorption cross sections have been measured recently by McGee and Burris (1987) at 295 and 210 K, between 300 and 324 nm, which is the wavelength region commonly used for atmospheric monitoring of SO_2.

OCS + hν → CO + S
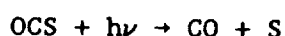
The absorption cross sections of OCS have been measured by Breckenridge and Taube (1970), who presented their 298 K results in graphical form, between 200 and 260 nm; by Rudolph and Inn (1981) between 200 and ~300 nm (see also Turco et al, 1981), at 297 and 195 K; by Leroy et al (1981) at 294 K, between 210 and 260 nm, using photographic plates; by Molina et al (1981) between 180 and 300 nm, at 295 and 225 K, and by Locker et al (1983) between 195 and 260 nm, in the 195 K to 403 K temperature range. The results are in good agreement in the regions of overlap, except for λ > 280 nm, where the cross section values reported by Rudolph and Inn (1981) are significantly larger than those reported by Molina et al (1981). The latter authors concluded that solar photodissociation of OCS in the troposphere occurs only to a negligible extent.

The recommended cross sections, given in Table 45, are taken from Molina et al (1981). (The original publication also lists a table with cross sections values averaged over 1 nm intervals, between 185 and 300 nm.)

The recommended quantum yield for photodissociation is 0.72. This value is taken from the work of Rudolph and Inn (1981), who measured the quantum yield for CO production in the 220-254 nm range.

CS_2 + hν → CS + S
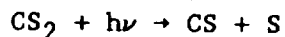
The CS_2 absorption spectrum is rather complex. Its photochemistry has been reviewed by Okabe (1978). There are two distinct regions in the near UV spectrum: a strong absorption extending from 185 to 230 nm, and a weaker one in the 290-380 nm range. The threshold wavelength for photodissociation is ~280 nm.

The photo-oxidation of CS_2 in the atmosphere has been discussed by Wine et al (1981d), who report that electronically excited CS_2 may react with O_2 to yield eventually OCS.

Table 45. Absorption Cross Sections of OCS

λ (nm)	$10^{20}\sigma(cm^2)$		λ (nm)	$10^{20}\sigma(cm^2)$	
	295 K	225 K		295 K	225 K
186.1	18.9	13.0	228.6	26.8	23.7
187.8	8.33	5.63	231.2	22.1	18.8
189.6	3.75	2.50	233.9	17.1	14.0
191.4	2.21	1.61	236.7	12.5	9.72
193.2	1.79	1.53	239.5	8.54	6.24
195.1	1.94	1.84	242.5	5.61	3.89
197.0	2.48	2.44	245.4	3.51	2.29
199.0	3.30	3.30	248.5	2.11	1.29
201.0	4.48	4.50	251.6	1.21	0.679
203.1	6.12	6.17	254.6	0.674	0.353
205.1	8.19	8.27	258.1	0.361	0.178
207.3	10.8	10.9	261.4	0.193	0.0900
209.4	14.1	14.2	264.9	0.0941	0.0419
211.6	17.6	17.6	268.5	0.0486	0.0199
213.9	21.8	21.8	272.1	0.0248	0.0101
216.2	25.5	25.3	275.9	0.0119	0.0048
218.6	28.2	27.7	279.7	0.0584	0.0021
221.5	30.5	29.4	283.7	0.0264	0.0009
223.5	31.9	29.5	287.8	0.0012	0.0005
226.0	30.2	27.4	292.0	0.0005	0.0002
			296.3	0.0002	-

Photodissociation quantum yield Φ - 0.72

NaCl + hν → Na + Cl
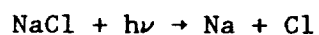
There are several studies of the UV absorption spectra of NaCl vapor. For a review of the earlier work, which was carried out at high temperatures, see Rowland and Rogers (1982). The recommended cross sections, listed in Table 46, are taken from the work of Silver et al (1986), who measured spectra of gas phase NaCl at room temperature in the range from ~190 to 360 nm, by directly monitoring the product Na atoms.

Table 46. Absorption Cross Sections of NaCl Vapor at 300 K

λ (nm)	$10^{20}\sigma$ (cm^2)
189.7	612
193.4	556
203.1	148
205.3	90.6
205.9	89.6
210.3	73.6
216.3	151
218.7	46.3
225.2	146
230.4	512
231.2	947
234.0	1300
237.6	638
241.4	674
248.4	129
251.6	251
254.8	424
260.2	433
268.3	174
277.0	40
291.8	0.8

NaOH + hν → Na + OH
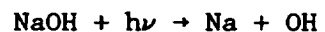
    The spectrum of NaOH vapor is poorly characterized. Rowland and Makide (1982) inferred the absorption cross section values and the average solar photodissociation rate from the flame measurements of Daidoji (1979). Additional measurements are required.

HETEROGENEOUS CHEMISTRY

We have attempted to present as much information on heterogeneous chemistry relevant to the stratosphere as is currently available. However, this is a new and rapidly developing field, and it is very complex compared to homogeneous chemistry. The problem is compounded by the difficulty in characterizing surfaces in terms of their area, phase identity, and composition. To a first approximation there are three particle types of concern: (1), the nitric acid trihydrate ($HNO_3 \cdot 3H_2O$), often called Type I because it is the first to form in the polar stratosphere; (2), crystals of pure water ice, called Type II because they are only stable in the stratosphere at significantly lower temperatures than required for Type I, and (3), the sulfuric acid aerosol, which is present at all latitudes and may affect stratospheric chemistry on a global basis. However, the extent of such effects is still unclear.

There is some doubt at the present time as to the exact composition of the Type I particles; i.e., whether they are pure $HNO_3 \cdot 3H_2O$ or have variable composition depending on the conditions of their formation. This is a vital question, because it is evident from experimental results that some of the most important properties, such as HCl solubilities, are strongly dependent on the amount of excess water in the particle. The nature of adsorption on such particles is currently in doubt, and it is not known whether surface adsorption or a true solid solution is involved. Further, since chemical processes may occur during the formation and possible re-evaporation of particles, surface properties may vary with time. All these factors make it very difficult to model the actual atmospheric particle chemistry with confidence.

For each of the three particle types mentioned above, the data (when available) are of four types:

(1) Sticking coefficients.

(2) Reaction probabilities.

(3) Solubility data.

(4) Equilibrium constants for particle formation.

The questions of how the data are to be used, and which data are the most important, depend on whether or not the gas-particle system is in equilibrium. That is, the treatment depends on the relative rates of competing processes, as for example the rate at which an adsorbed species undergoes desorption compared to the rate at which it undergoes reaction.

Sticking Coefficients

Sticking coefficients are listed in Table 47. These are experimental data as reported by the researchers themselves, and we have not attempted to recommend a "preferred value". The coefficients are defined as the fraction of collisions of a gaseous species with a particle which result in retention of the colliding species with its original chemical identity.

In this context ionization would not be considered a change in chemical identity. Laboratory measurements of sticking coefficients should refer to the "zero time" value, because as the system approaches saturation the apparent value will decline when desorption becomes competitive. However, some of the data in Table 47 may not have been taken under true zero time conditions, and would therefore only be lower limits to the correct values.

Reaction Probabilities

The available data on reaction probabilities are listed in Table 48. As with the sticking coefficient data, we have not recommended a preferred value. The coefficients are defined as the fraction of collisions which result in immediate chemical conversion of the colliding species, followed by either retention or emission of the newly-formed products.

Solubility Data

For the present, the solubility data listed in Table 49 are limited to gas-liquid equilibria. Although some measurements have been reported for solid particles, such as for the HCl-Type I and Type II systems (Hanson and Mauersberger, 1988a,b), the effective Henry's law constants in those studies depend on various experimental conditions, such as the quantity of substrate employed. Therefore it is not useful to apply those results to atmospheric particles. The concept of gas-solid solubility may not be strictly applicable to atmospheric particles. For liquid droplets the situation is probably more straightforward, because diffusion in the liquid forces adherence to solubility limits, as well as maintaining equilibrium with the gas phase concentration.

Equilibrium Constants for Particle Formation

Gas-solid equilibria such as those involved in the formation of ice and the hydrates of nitric acid can be represented as temperature dependent equilibrium constants. Some data of this type are shown in Table 50, primarily for nitric acid hydrates. For Type II particles, the data are tabulated in standard references as the vapor pressure of ice, and are not reproduced here.

The equilibrium constants are represented in the form $K_c = A \exp(B/T)$, where K_c has the dimensions $(molec/cm^3)^n$, with n being the number of gaseous molecules forming the hydrate. The quantities A and B are related to the thermodynamic quantities $\Delta S°$ and $\Delta H°$ as follows (standard state of one atmosphere):

$$A = (N/eR'T)^n \exp(\Delta S°/R)$$

$$B = -\Delta H°/R + nT$$

Table 47. Sticking Coefficients on Particle Surfaces

Water-H_2SO_4 Particles

Species	Sticking Coefficient	T(K)	Wt. % H_2SO_4	Reference
HCl	>0.016	198	55	Tolbert et al, 1990
	≥0.003[a]	203	60	Tolbert et al, 1990
	<7x10^{-5}	218	70	Tolbert et al, 1990
	<7x10^{-5}	208	70	Tolbert et al, 1990
	0.3	193	25	Leu et al, 1989
	0.06	193	50	Leu et al, 1989
	<0.001	193	58	Leu et al, 1989
	<0.0001	193	65	Leu et al, 1989
	<0.0001	193	72	Leu et al, 1989
	<0.0001	193	78	Leu et al, 1989
	0.146	283	20	Watson et al, 1989
	0.163	283	36	Watson et al, 1989
	0.151	283	40	Watson et al, 1989
	≥0.104[a]	283	47	Watson et al, 1989
	≥0.079[a]	283	52	Watson et al, 1989
	≥0.004[a]	283	58	Watson et al, 1989
HNO$_3$	0.07	223	40	Tolbert et al, 1990
	0.07	225	50	Tolbert et al, 1990
	≥0.1[a]	223	58	Tolbert et al, 1990
	≥0.2[a]	206	58	Tolbert et al, 1990
	0.3	195	58	Tolbert et al, 1990
	≥0.1[a]	223	65	Tolbert et al, 1990
	≥0.3[a]	208	65	Tolbert et al, 1990
	≥0.3[a]	199	65	Tolbert et al, 1990
	≥0.05[a]	229	74	Tolbert et al, 1990
	≥0.1[a]	208	74	Tolbert et al, 1990
	≥0.25[a]	193	74	Tolbert et al, 1990
	≥0.007[a]	238	87	Tolbert et al, 1990
	≥0.014[a]	218	87	Tolbert et al, 1990
	≥0.02[a]	188	87	Tolbert et al, 1990
	≥0.11[a]	283	73	Van Doren et al, 1990
NO	<1.0x10^{-6}	298	96	Baldwin and Golden, 1979
NO$_2$	<1.0x10^{-6}	298	96	Baldwin and Golden, 1979
O$_3$	<1.0x10^{-6}	298	96	Baldwin and Golden, 1979
H$_2$O$_2$	7.8x10^{-4}	298	96	Baldwin and Golden, 1979
SO$_2$	<1.0x10^{-6}	298	96	Baldwin and Golden, 1979

[a] Lower limit indicates that experimental sticking coefficient is believed to be solubility limited.

Table 47. (Continued)

Water Ice Particles

Species	Sticking Coefficient	T(K)	Reference
H_2O	$0.3^{+0.7}_{-0.1}$	200	Leu, 1988a
HCl	$0.4^{+0.6}_{-0.2}$	200	Leu, 1988a
	0.26 ± 0.04	198	Tolbert et al, 1989
	>0.05	200	Molina et al, 1987
	0.18^a	274	Van Doren et al, 1990b
Cl_2	<0.0001	200	Leu, 1988a
ClO	>0.01	195	Leu, 1988b
HNO_3	$0.3^{+0.7}_{-0.1}$	200	Leu, 1988a
	0.16^a	268	Van Doren et al, 1990a
NO	<0.0001	195	Leu, 1988b
NO_2	<0.0001	195	Leu, 1988b
O_3	<0.0001	195	Leu, 1988b
CH_3Cl	<0.0001	195	Leu, priv. comm., 1988
H_2O_2	0.18^a	273	Worsnop et al, 1989
SO_2	0.11^a	273	Worsnop et al, 1989

[a] Liquid water droplet. These sticking coefficients show a strong negative temperature dependence. Direct extrapolation indicates sticking coefficient will approach unity at stratospheric temperatures.

Table 47.   (Continued)

Water-HNO3 Surfaces

Species	Sticking Coefficient	T(K)	Wt. % HNO$_3$	Reference
HCl	0.06	196	44	Moore et al, 1989
	0.05	196	46	Moore et al, 1989
	0.03	196	48	Moore et al, 1989
	0.02	196	50	Moore et al, 1989
	0.005	196	52	Moore et al, 1989
	0.0008	196	54	Moore et al, 1989
	0.0001	196	56	Moore et al, 1989
	<0.00001	196	58	Moore et al, 1989
	0.08	198	47	Tolbert et al, 1989
	0.0001	198	65	Tolbert et al, 1989
	<0.00001	198	70	Tolbert et al, 1989

Table 48. Reaction Probabilities on Particle Surfaces

Water-H_2SO_4 Particles

Species	Reaction Probability	T(K)	Wt. % H_2SO_4	HCl Mole Fraction	Reference
$ClONO_2$	0.0026	210	65	0.0	Tolbert et al, 1988b
	0.0003	210	65	0.0002	Tolbert et al, 1988b
	0.0003	230	75	0.0	Tolbert et al, 1988b
	0.00032	295	96.5	0.0	Rossi et al, 1987
ClO	0.008	190	75	0.0	Martin et al, 1980
N_2O_5	>3.8×10^{-5}	298	96	0.0	Baldwin and Golden, 1979
	0.06	283	73	0.0	Van Doren et al, 1990b
	0.14	273	64-77[a]	0.0	Mozurkewich and Calvert, 1988
	0.10	293	64-77[a]	0.0	Mozurkewich and Calvert, 1988

[a] Estimated from relative humidity measurements.

Table 48. (Continued)

Water Ice Particles

Species	Reaction Probability	T(K)	HCl Mole Fraction	Reference
$ClONO_2$	0.009±0.002	185	0.0	Tolbert et al, 1987
	0.06±0.03	200	0.0	Leu, 1988a
	$0.27^{+0.73}_{-0.13}$	200	0.02-0.07	Leu, 1988a
	0.02	200	0.0	Molina et al, 1987
	0.05-0.1	200	0.0035-0.01	Molina et al, 1987
N_2O_5	>0.003	185	0.07-0.14	Tolbert et al, 1988a
	>0.001	185	0.0	Tolbert et al, 1988a
	0.01-0.03	188	0.0	Quinlan et al, 1989
	0.028±0.011	195	0.0	Leu, 1988b
	0.056	195	0.015-0.04	Leu, 1988b
	0.06[a]	271	0.0	Van Doren et al, 1990a

[a] Liquid water droplet. Sticking coefficient shows strong negative temperature dependence. Direct extrapolation indicates sticking coefficient will approach unity at stratospheric temperatures.

Table 48. (Continued)

<u>Water-HNO₃ Particles</u>

Species	Reaction Probability	T(K)	Wt. % HNO$_3$	HCl Mole Fraction	Reference
ClONO$_2$	0.03	196	42	0.0	Moore <u>et al</u>, 1989
	0.02	196	46	0.0	Moore <u>et al</u>, 1989
	0.012	196	48	0.0	Moore <u>et al</u>, 1989
	0.006	196	50	0.0	Moore <u>et al</u>, 1989
	0.0014	196	52	0.0	Moore <u>et al</u>, 1989
	0.0003	196	54	0.0	Moore <u>et al</u>, 1989
	0.00007	196	56	0.0	Moore <u>et al</u>, 1989
	0.07-1.0	196	42-54	0.03-4.0	Moore <u>et al</u>, 1989
N$_2$O$_5$	0.015±0.006	188		0.0	Quinlan <u>et al</u>, 1989

Table 49. Henry's Law Constants for Gas-Liquid Solubilities

	A (M/atm)	B (K)	H(T) (M/atm)		Note
Nitric Acid in Sulfuric Acid					
% H_2SO_4					
87	3.56×10^{-3}	3320	1.3×10^4	(220K)	1
74	8.54×10^{-3}	3550	8.7×10^4	(220K)	1
66	2.02×10^{-1}	3190	4.0×10^5	(220K)	1
58	7.47×10^{-8}	7160	1.0×10^7	(220K)	1
73	-	-	5.0×10^3	(283K)	2
HCl in Sulfuric Acid					
% H_2SO_4					
60	-	-	$> 8.6 \times 10^3$	(203K)	3
40	-	-	$> 1.0 \times 10^4$	(283K)	4
50	-	-	$> 1.0 \times 10^3$	(283K)	4
60	-	-	$> 1.0 \times 10^2$	(283K)	4
70	-	-	$> 1.0 \times 10^1$	(283K)	4

$H(M/atm) = A \exp(B/T)$.

NOTES TO TABLE 49

1. These parameters are from measurements of Reihs et al (1990) in the temperature range 188-240K. Extrapolation to higher temperatures shows good agreement with other studies (Watson et al, 1989).

2. High temperature value from Van Doren et al (1990b). Estimated from decrease in HNO_3 uptake and gaseous evolution of HNO_3 from N_2O_5 uptake.

3. From Tolbert (1989, private communication); see Watson et al, 1989.

4. From Watson et al (1989). Estimated by assuming HCl uptake is solubility limited as calculated from Hammett acidity of aqueous sulfuric acid. Effective solubility given by

where

$$H^* = HK_a/10^{-Ho}$$

$HK_a = 10^7$ M/atm at 283 K
$H_o = -3$ at 40 wt%
$H_o = -6$ at 70 wt%

See discussion in Watson et al (1989), Clegg and Brimblecombe (1986), and Schwartz (1988).

Table 50. Equilibrium Constants for Solid Hydrate Formation

Reaction	Log(A)	B ± ΔB/K	K(200)	f	Note
$(HNO_3 \cdot 3H_2O)_s \rightarrow HNO_3 + 3H_2O$	109.2	-27100±1000	2.3×10^{50}	10	1
$(HNO_3 \cdot H_2O)_s \rightarrow HNO_3 + H_2O$	58.7	-15500±1500	1.1×10^{25}	20	1

(a) $K = A \exp(B/T)$; units are $(molec/cm^3)^n$ where n is the number of molecules in the hydrate.

(b) The factor f is the estimated uncertainty in the temperature range of interest; i.e., about 190-200K.

NOTES TO TABLE 50

1. These parameters are based on the analysis by Smith (1990) of $HNO_3 \cdot 3H_2O$ vapor pressure data of Hanson and Mauersberger (1988a,b). They are consistent with the free energies of formation of the hydrates as measured by Forsythe and Giauque (1942). The corresponding enthalpies of formation at temperatures near 200 K are:

$$\Delta H_f(HNO_3 \cdot 3H_2O) = -260 + 4 \text{ kcal/mole}$$

$$\Delta H_f(HNO_3 \cdot H_2O) = -121 \pm 4 \text{ kcal/mole}$$

$$S^\circ(HNO_3 \cdot 3H_2O) = 35 \pm 4 \text{ cal/K-mole}$$

$$S^\circ(HNO_3 \cdot H_2O) = 7 \pm 4 \text{ cal/K-mole}$$

APPENDIX.

GAS PHASE ENTHALPY DATA

The following data are adapted mainly from CODATA (1984), although a few entries have been updated.

SPECIES	$\Delta H_f(298)$ (Kcal/mol)	SPECIES	$\Delta H_f(298)$ (Kcal/mol)	SPECIES	$\Delta H_f(298)$ (Kcal/mol)	SPECIES	$\Delta H_f(298)$ (Kcal/mol)
H	52.1	CH_3OH	-48.2	F_2	0.00	CH_3Cl	-19.6
H_2	0.00	CH_3OOH	-31.3	HF	-65.34	ClCO	-5±1
O	59.57	CH_3ONO	-15.6	HOF	-23.4±1	$COCl_2$	-52.6
$O(^1D)$	104.9	CH_3ONO_2	-28.6	FO	26±5	CHFCl	-14.5±2
O_2	0.00	$CH_3O_2NO_2$	-10.6±2	F_2O	5.9±.4	CH_2FCl	-63±2
$O_2(^1\text{-DELTA})$	22.5	C_2H	135.0	FO_2	6±1	CFCl	7±6
$O_2(^1\text{-SIGMA})$	37.5	C_2H_2	54.35	F_2O_2	5±2	$CFCl_2$	-22±2
O_3	34.1	C_2H_3	68.1	FONO	-15±7	$CFCl_3$	-68.1
HO	9.3	C_2H_4	12.45	FNO	-16±2	CF_2Cl	-64±3
HO_2	3±1	C_2H_5	28.4	FNO_2	-26±2	CF_2Cl_2	-117.9
H_2O	-57.81	C_2H_6	-20.0	$FONO_2$	2.5±7	CF_3Cl	-169.2
H_2O_2	-32.60	CH_2CN	58.6	CF_2	-44±2	$CHFCl_2$	-68.1
N	113.00	CH_3CN	19.1	CF_3	-112±1	CHF_2Cl	-115.6
N_2	0.00	CH_2CO	-14.23	CF_4	-223.0	COFCl	-102±2
NH	82.0	CH_3CO	-5.8	CHF_3	-166.8	CH_2CF_3	-124±2
NH_2	45.3	CH_3CHO	-39.7	CHF_2	-58±2	CH_3CF_2	-72±2
NH_3	-10.98	C_2H_5O	-4.1	CH_2F_2	-107.2	CH_3CF_3	-178
NO	21.57	CH_2CH_2OH	-13±2	CH_2F	-8±2	CF_2CF_3	-213
NO_2	7.9	C_2H_5OH	-56.2	CH_3F	-55.9±1	CHF_2CF_3	-264
NO_3	17±2	CH_3CO_2	-49.6	FCO	-41±14	C_2Cl_4	-3.0
N_2O	19.61	$C_2H_5O_2$	-4±3	COF_2	-151.7	C_2HCl_3	-1.9
N_2O_3	19.8	CH_3OOCH_3	-30.0	Cl	28.9	CH_2CCl_3	11±7
N_2O_4	2.2	C_3H_5	39.4	Cl_2	0.00	CH_3CCl_3	-34.0
N_2O_5	2.7±2	C_3H_6	4.8	HCl	-22.06	CH_2CH_2Cl	19.3±2
HNO	23.8	$n\text{-}C_3H_7$	22.6±2	ClO	24.4	Br	26.7
HONO	-19.0	$i\text{-}C_3H_7$	19±2	ClOO	23±1	Br_2	7.39
HNO_3	-32.3	C_3H_8	-24.8	OClO	23±2	HBr	-8.67
HO_2NO_2	-11±2	C_2H_5CHO	-44.8	$ClOO_2$	>13.4	HOBr	-19±2
C	170.9	CH_3COCH_3	-51.9	ClO_3	37	BrO	30
CH	142.0	S	66.22	Cl_2O	19.5	BrNO	19.7
CH_2	92.3	S_2	30.72	Cl_2O_2	31±3	BrONO	25±7
CH_3	35.1	HS	34±1	Cl_2O_3	34±3	$BrONO_2$	12±5
CH_4	-17.88	H_2S	-4.9	HOCl	-18.6±3	BrCl	3.5
CN	104.0	SO	1.2	ClNO	12.4	CH_2Br	40±2
HCN	32.3	SO_2	-70.96	$ClNO_2$	3.0	$CHBr_2$	45±2
CH_3NH_2	-5.5	SO_3	-94.6	ClONO	20±7	CH_2Br_2	-2.6±2
NCO	38	HSO	1±3	$ClONO_2$	5.5	CH_3Br	-8.5
CO	-26.42	HSO_3	-92±2	FCl	-12.1	I	25.52
CO_2	-94.07	CS	65	CCl	120±5	I_2	14.92
HCO	9.0	CS_2	28.0	CCl_2	57±5	HI	6.3
CH_2O	-26.0	CH_3S	33±2	CCl_3	18±1	CH_3I	3.5
COOH	-50±2	CH_3SH	-5.5	CCl_4	-22.9	CH_2I	54.9±2
HCOOH	-90.5	CH_3SCH_3	-8.9	$CHCl_3$	-24.6	IO	41.1
CH_3O	3.5	CH_3SSCH_3	-5.8	$CHCl_2$	23±2	INO	29.0
CH_3O_2	5±2	OCS	-34	CH_2Cl	29±2	INO_2	14.4
CH_2OH	-6.2	F	18.98	CH_2Cl_2	-22.8		

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